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## ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

**3271. Accuracy and reproducibility of chemical analysis.** A. K. Babko (*Zavod. Lab.*, 1955, **21** [3], 269-277).—Many examples are quoted to show that applications of statistics to the results of chemical analysis are made without proper consideration of inherent chemical errors of methods. The mean of the results obtained by a number of laboratories has no special claim to be the true result. It is recommended, to avoid needlessly complicated calculations in statistical analysis, that the average error be calculated and transformed to a figure representing approximately the standard deviation by multiplying it by 1.25. The average error is the arithmetical mean of the absolute values of the individual deviations from the mean of the results. G. S. SMITH

**3272. Thermal stability of analytical standards.** C. Duval (*Anal. Chim. Acta*, 1955, **13** [1], 32-37).—Various substances used as analytical standards are examined for their thermal stability, and infrared lines are given to assist in the identification of pure specimens. Sodium carbonate loses any moisture it may contain at 100° C, and is then stable up to 840° C. Sodium bicarbonate is stable up to 79° C, and the change into  $\text{Na}_2\text{CO}_3$  is complete at 186° C. Sodium acetate trihydrate loses  $\text{H}_2\text{O}$  even at room temp.; dehydration is complete at 170° C, after which the salt is stable up to 440° C. Commercial cryst. borax is stable up to  $\approx 35^\circ\text{C}$ , and is not anhydrous until  $\approx 525^\circ\text{C}$ . As the water content is not strictly  $10\text{H}_2\text{O}$ , the use of borax in accurate work is not advisable. Commercial samples of  $\text{Na}_2\text{HPO}_4$  contain  $< 12\text{H}_2\text{O}$ . The salt is anhydrous at 180° C and is stable up to at least 280° C; before use, it should be dried between 180° and 280° C. The hydration of commercial  $\text{Na}_2\text{PO}_4$  is variable, and may correspond to a mixture. The use of the anhydrous salt, which is formed above 230° C, is recommended. Sodium potassium tartrate has no horizontal portion in its thermolysis curve, and its use in accurate work is not advisable. The monohydrate of ammonium oxalate is stable below 65° C, but the degree of hydration is only approx. unity. It becomes anhyd. at 133° C, and is then stable up to 182° C. The use of the anhyd. salt is recommended. It is confirmed that K H phthalate is stable up to 240° C. Lithium carbonate is stable from room temp. to 428° C. Hydrated  $\text{BaCl}_2$  cannot be employed as an accurate standard for water in the Karl Fischer method, since it appears to be a mixture of the mono- and di-hydrates. For other work the anhyd. salt, which is stable from 150° to 875° C, is recommended. Potassium dichromate is always truly anhyd. and is stable up to  $\approx 650^\circ\text{C}$ . J. H. WATON

**3273. Selectivity and specificity of organic reagents.** G. J. Henning (*Chem. Weekbl.*, 1955, **51** [28], 519-527).—A review is given of work on

the connection between the analytical properties of an org. reagent and the stability of the metal ion complex formed. Factors affecting the stability, such as changes in the nature of the bonds, and the different effects of metal ions, are considered.

A. J. MEE

**3274. Thioacetamide in analytical chemistry.** H. Flaschka (*Chemist Analyst*, 1955, **44** [1], 2-7).—The uses of thioacetamide in analysis as an alternative to gaseous  $\text{H}_2\text{S}$  are reviewed. Among the advantages described is the possibility of effecting separations in the presence of EDTA, which are not possible when gaseous  $\text{H}_2\text{S}$  is used. D. LIFF

**3275. New substitutes for the Zimmermann-Reinhardt reagent.** K. M. Somasundaram and C. V. Suryanarayana (*J. Indian Chem. Soc.*, 1955, **32** [1], 45-48).—Addition of a solution of either sodium acetate or borax to the reaction mixture in the permanganate titration of Fe in HCl solution has been found to yield the same values as those obtained by the Zimmermann-Reinhardt reagent (I) or for  $\text{Fe}^{++}$  in  $\text{H}_2\text{SO}_4$ . Advantages of the new reagents over I are easier preparation, sharper end-point, and duration of end-point of  $1\frac{1}{2}$  min., compared with  $\frac{1}{2}$  min. for I. (*Cf. Anal. Abstr.*, 1954, **1**, 1843.) O. M. WHITTON

**3276. Substituted thiocarbazones. Synthesis and properties of asymmetrical derivatives of thiocarbazone.** L. S. Pupko and P. S. Pel'kis (*Zh. Obshch. Khim.*, 1954, **24**, 1640-1645).—Dithione derivatives are synthesised from aniline as follows:  
 $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{N:NCl} (+ \text{CH}_3\text{NO}_2) \rightarrow$   
 $\text{C}_6\text{H}_5\text{N:N-CH}_2\text{NO}_2 (+ \text{RN:NCl}) \rightarrow$   
 $\text{C}_6\text{H}_5\text{N:N-CH(NO}_2\text{):N:NR} [+ (\text{NH}_4)_2\text{S}] \rightarrow$   
 $\text{C}_6\text{H}_5\text{NH-NH-C(NH}_2\text{)(SH)-NH-NHR} \rightarrow$   
 $\text{C}_6\text{H}_5\text{NH-NH-CS-NH-NHR}$   
 $\text{C}_6\text{H}_5\text{N:N-CS-NH-NHR}$  or  $\text{C}_6\text{H}_5\text{NH-NH-CS-N:NR}$ ,  
 where R is *o*-, *m*- or *p*- $\text{C}_6\text{H}_4\text{CH}_3$ -, *o*-, *m*- or *p*- $\text{CH}_2\text{O-C}_6\text{H}_4$ -, *o*- $\text{C}_6\text{H}_4\text{O-C}_6\text{H}_4$ - or 1:2:4- $\text{C}_6\text{H}_2\text{Br}_3$ -. Benzene solutions of intramolecular complexes of these products with ions of Pb, Hg, Zn and Ag have a single absorption max. in the short-wave region, at longer wavelengths than those with dithione. R. TRUSCOE

**3277. Estimation of metals as sulphides. IV. Atmospheric oxidation of alkali sulphides.** I. K. Taimni and G. B. S. Salaria (*Anal. Chim. Acta*, 1955, **13** [1], 28-31).—Alkali sulphide soln. prepared by passing  $\text{H}_2\text{S}$  into soln. of alkalis for 2 to 4 min. at  $< 5^\circ\text{C}$  are stable for a considerable time. These soln. are therefore suitable reagents for the quant. pptn. of metals as sulphides, since the ppt. is free from elementary S. J. H. WATON

**3278. Sodium chloride as standard titrimetric substance in alkalimetry.** C. W. Naumann (*Chem. Tech., Berlin*, 1954, **6** [10], 545).—Standard solutions of HCl (0.05 to 0.02 N) are produced by passing NaCl solutions of equivalent concn. through H-ion

exchange columns containing Wofatit F (50 ml) above glass wool (lower 50 ml of column). The adsorption capacity permits filtration (at 2 drops per sec.) of 500 ml of 0.05 N NaCl; the Wofatit (H) is regenerated by washing with 5 to 7 per cent. HCl and then distilled water until the filtrate is neutral to methyl orange.

D. R. GLASSON

### 3279. Redox titrations with luminescent indicators.

**I. Determination with hydrogen peroxide.** L. Erdey and I. Buzás (*Acta Chim. Hung.*, 1955, **6** [1-2], 77-91).—Excess of oxidising agent will produce a visible chemiluminescence with luminol (3-aminophthalhydrazide) and other substances, so that the appearance of luminescence can be used to show the end-point of a redox titration. A special burette control is described for ease of operation in the dark. Good results are obtained for the titration of  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{ClO}^-$  and  $\text{BrO}^-$  with 0.1 N  $\text{H}_2\text{O}_2$  in hot alkaline solution in the presence of 1 ml of 0.5 per cent. lucigenin (10:10'-dimethyl-9:9'-diacridinium dinitrate) per 100 ml. The determination of  $\text{Cr}^{+++}$  can be effected by oxidation with an excess of NaBrO and titration of the excess of  $\text{BrO}^-$ .

**II. Determination with sodium hypobromite.** (*Ibid.*, 1955, **6** [1-2], 93-114).—The titration of  $\text{AsO}_3^{3-}$ ,  $\text{SbO}_3^{3-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$  and  $\text{SCN}^-$  can be carried out with 0.1 N or 0.01 N NaBrO in alkaline solution, using 3 ml of 0.01 or 0.001 per cent. luminol as luminescent indicator. The method is specially suitable for turbid or coloured solutions.

**III. Determination with sodium hypochlorite.** (*Ibid.*, 1955, **6** [1-2], 115-122).—The titration of  $\text{AsO}_3^{3-}$ ,  $\text{SbO}_3^{3-}$  and  $\text{S}_2\text{O}_3^{2-}$  in alkaline solution and  $\text{N}_2\text{H}_4$  at pH 7 can be effected hot with alkaline 0.1 N NaClO, using 10 ml of 0.01 per cent. luminol. The reaction is slower with NaClO than with HBrO, and it is necessary to titrate until the luminescence persists for 2 to 5 min. The results, except for those for  $\text{AsO}_3^{3-}$ , are less accurate than with NaBrO.

**IV. Determination with sodium arsenite.** (*Ibid.*, 1955, **6** [1-2], 123-126).—Titrations of  $\text{ClO}^-$  and  $\text{BrO}^-$  can be carried out in alkaline solution with 0.1 N  $\text{As}_2\text{O}_3$  solution containing 0.001 per cent. of luminol. The  $\text{As}_2\text{O}_3$  solution is added until a drop no longer produces a flash of light. No interference is given by  $\text{ClO}_2^-$ ,  $\text{ClO}_2$  or  $\text{BrO}_2^-$ .

**V. Determination with hydrazine sulphate.** (*Ibid.*, 1955, **6** [1-2], 127-130).—Lucigenin is chemiluminescent with  $\text{H}_2\text{O}_2$ , but not with  $\text{ClO}^-$  or  $\text{BrO}^-$ . In alkaline solution, in the presence of air,  $\text{N}_2\text{H}_4$  decomposes with formation of  $\text{H}_2\text{O}_2$ . Thus alkaline soln. of  $\text{ClO}^-$  and  $\text{BrO}^-$  can be titrated with a feebly acid 0.1 N solution of  $\text{N}_2\text{H}_4$ , with 1 ml of 0.5 per cent. lucigenin as luminescent indicator.

A. B. DENSHAM

### 3280. Spectral analysis of non-conducting powders.

G. A. Monnot (*Mikrochim. Acta*, 1955, [2-3], 446-466).—Ultra-violet emission and i.r. absorption methods are used in the control of purity of powders used in animal tests in research on pneumoconiosis (composition of coal ashes, schists, etc.). Systematic use of the tableting of fine powders with KBr allows their investigation in i.r. from 2 to 15  $\mu$ , e.g., in the determination of quartz, calcite, etc. The application of u.v. absorption to the study of silicic acids prepared in various ways is demonstrated.

D. R. GLASSON

**3281. Methodology of the study of standards for spectrographic analysis.** A. B. Shaeovich (*Zavod. Lab.*, 1955, **21** [3], 332-336).—It is recommended that standards for spectrographic analysis should

have their composition established not by chemical analysis but spectrographically by the use of primary synthetic standards in the form of solutions. The use of the sparking device (fulgurator) described is stated to give errors of only  $\pm 3$  per cent.

G. S. SMITH

**3282. Origin of errors in the spectrographic analysis of ores.** V. V. Nédler (*Zavod. Lab.*, 1955, **21** [3], 307-310).—Errors in the results of spectrographic analysis of ores are due mainly to differences between the composition of the standards and that of the samples. With the determination of Pb in ores with added Bi, considerable changes occur in the relative intensities of the lines Pb 2833 Å and Bi 2898 Å with additions of 10 per cent. of  $\text{Na}_2\text{CO}_3$  or 10 per cent. of  $\text{Fe}_2\text{O}_3$ . It is shown that these changes cannot be accounted for by temp. and ionisation factors, and the causes are still unexplained.

G. S. SMITH

**3283. The use of alcoholic solutions in flame-spectrophotometric analysis.** A. Fink (*Mikrochim. Acta*, 1955, [2-3], 314-328).—The accuracy and sensitivity of simple flame photometers in the determination of Ca and Mg are considerably increased by using alcoholic solutions of several of their salts, notably the nitrates and chlorides of Ca and Mg, and  $\text{MgSO}_4$ . The line emission increases with increasing heats of combination of the homologous alcohols, e.g., from methyl to pentyl. The photocurrent of the selenium cell increases threefold when isopentanol is used as solvent instead of water. A Lange flame photometer has been remodelled for the spraying of combustible liquid samples. Very small amounts of  $\text{Ca}(\text{NO}_3)_2$  in technical products have been determined; the reproducibility is within 1 per cent. and the error is  $\pm 0.02$  per cent. of  $\text{Ca}(\text{NO}_3)_2$ . Results for Mg are not so favourable.

D. R. GLASSON

**3284. Recent progress in the study of the far ultra-violet.** B. Vodar and J. Romand (*Mikrochim. Acta*, 1955, [2-3], 429-445).—Current methods and possible developments of spectroscopy of radiations in the far u.v., which are absorbed by air, are reviewed. Sources of radiation are described; Lyman's, essentially the discharge of a condenser in a gas across a capillary tube, is the only source giving a continuous spectrum in all the u.v. range. Discontinuous spectra are obtainable by using maintained discharges as in a hydrogen lamp. Electrodes of Cu, Fe and U on C are described and the spectra shown. Optical materials of suitable transparency are quartz,  $\text{Al}_2\text{O}_3$  (white sapphire),  $\text{CaF}_2$  and LiF. Thin films of SiO are promising. Photographic emulsions containing Na salicylate are also recommended. The disposition of apparatus for photographic photometry in the far u.v. is illustrated. The absorbent may be heated to 900°C or cooled to the temp. of liq. hydrogen. The spectra of water vapour at 900°C in the Schumann region, and of solid benzene,  $\text{O}_2$  and  $\text{N}_2\text{O}$  at low temp. have all been recorded. For photo-electric spectrophotometry in this region, a special monochromator is described, and fluorescent and direct-recording methods are compared; use of a Cu-Be photomultiplier is often advantageous. Quant. analysis of metalloids is possible in this spectral region.

D. R. GLASSON

**3285. Analysis of solutions containing two reducible substances by polarography and coulometry at controlled potential.** L. Meites (*Anal. Chem.*, 1955, **27** [7], 1114-1116).—A new procedure

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applicable to the determination of two substances that give overlapping or even coincident polarographic waves involves the polarographic measurement of the total diffusion current of the combined wave and the determination, by coulometry at controlled potential, of the total number of milliequiv. of reducible material in a known vol. of the soln. The theory of the method is presented and the experimental error is shown to become serious when the ratio of the two diffusion coeff. falls below  $\approx 1.8$ , the present method becoming invalid when this ratio becomes  $< 1.4$ . Data obtained in analyses of mixtures of  $Tl^+$  and  $Pb^{2+}$  in 1 M HCl as supporting electrolyte are reported; the mean error was  $\pm 1.3$  per cent.

W. J. BAKER

**3286. Radioactive tracing. V. The preparation and assay of labelled compounds.** F. P. W. Winterringham (*Lab. Practice*, 1955, **4** [7], 288-292).—Techniques for accurate radioactivity measurement of prepared gas, liquid or solid samples under standard conditions of geometry are discussed, and some apparatus used is illustrated. Tritium-labelled samples are assayed by converting into water by dry oxidation with O at 1000°C. The water is then converted into a suitable counting C, e.g., tritiated hydrogen, by treatment with lithium aluminium hydride dissolved in anhydrous diethylene glycol monoethyl ether. Carbon-14 labelled gases are assayed by recovering the C as labelled  $CO_2$  by wet or dry oxidation of the sample and precipitating as barium or calcium carbonate. Carbon dioxide is quantitatively recovered by adding acid to the carbonate or heating it with lead chloride. The assay of  $^{41}A$  and  $^{85}Kr$  is discussed briefly. The assay of  $^{14}C$  in solid samples by quantitative recovery as  $CO_2$  by wet or dry oxidation of the sample is described. The  $CO_2$  is absorbed in alkaline solution and the carbonate formed is precipitated, by adding slightly alkaline  $CaCl_2$ , as a flat disc of  $CaCO_3$ . The precipitate is washed with ether, dried and treated with a neutral solution of cellulose nitrate in amyl acetate. The final weighings and counting rate are a measure of the total C and  $^{14}C$  contents of the original sample. For doubly labelled compounds, such as  $^{14}CH_3^{13}I$ , the C is absorbed as  $CO_2$  in N NaOH, and the halogen in alkaline N  $NaMnO_4$  and in N NaOH containing 0.3 M hydrazine. Reference is made to the assay of radiocobalt as the ferrocyanide, radio-calcium as the carbonate or oxalate, radio-arsenic as the metal, radiophosphorus as magnesium ammonium phosphate, radiosulphur as barium sulphate or as benzidine sulphate, and the radio-halogens as the silver salts. A general counting procedure is given.

O. M. WHITTON

See also Abstract 3406.

## 2.—INORGANIC ANALYSIS

**3287. Metallurgical analysis: some physico-chemical considerations of precipitation reactions and electrolytic separations.** C. E. A. Shanahan (*Metallurgia*, 1955, **51**, 255-261).—The physico-chemical principles underlying reactions that involve the formation of ppt. of sulphides, hydroxides, etc., and electrolytic separation techniques, e.g., the mercury-cathode process often used in the determination of Al in steel, are discussed from the viewpoint of the metallurgical analyst.

G. C. JONES

**3288. Oscillographic polarograms of simple metal ions.** I. I. Tsapiv (*Zavod. Lab.*, 1955, **21** [3], 286-289).—The oscillographic polarograph described previously (*Ibid.*, 1952, **18**, 7) is applied to the determination of Cu, Cd and Pb. Silver electrodes are used in a medium of 0.5 or 1 N KCl, and the potential is applied in separate triangular impulses with a ratio between the duration and period of 0.72 to 0.80.

G. S. SMITH

**3289. Flame-photometric determination of lithium in silicate rocks.** R. B. Ellestad and E. L. Horstman (*Anal. Chem.*, 1955, **27** [8], 1229-1231).—From 0.001 to 0.03 per cent. of  $Li_2O$  in silicate rocks and minerals can be determined by flame photometry of the soln. (containing alkali metals and Mg) obtained after acid decomposition of the sample (0.5 g), followed by a single pptn. with excess of pure basic lead carbonate. An aliquot of this soln. is burned in a special flame attachment to a Beckman DU spectrophotometer, measurement being made at 671 m $\mu$  and a slit-width of 0.4 mm. Continuum and radiation interference by Na<sup>+</sup> and K<sup>+</sup> are compensated by additions to the Li standards of concn. of Na<sup>+</sup> and K<sup>+</sup> equal to those in the sample. The sensitivity of the method is 0.05 p.p.m. of  $Li_2O$  in soln., equiv. to 0.0005 per cent. of  $Li_2O$  in the sample, whilst the accuracy is  $\pm 0.001$  per cent.

W. J. BAKER

**3290. Syntheses and uses of new analytical reagents for potassium. I. "Dihexyl."** M. Ishibashi and K. Tōei (*J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** [1], 104-106).—m-Di(nitro-anilino)benzene was prepared from m-phenylenediamine and chlorotrinitrobenzene in ethanol as orange crystals, and nitrated with fuming  $HNO_3$  and conc.  $H_2SO_4$  to give "dihexyl" [4:6-dinitro-1:3-di(trinitroanilino)benzene] (I). The solubility of the potassium salt of I was measured at 0° to 40°C and was found to be greater (0.7 g per litre at 0°C) than that of the potassium salt of dipicrylamine (II), showing that I is inferior to II as the reagent. The limit of detection of K in a pure solution is 2 g of K per litre. II. "α-Hexyl." K. Tōei (*Ibid.*, 1955, **76** [1], 106-110).—"α-Hexyl" [2:4-dinitro-N-(2:4:6-trinitrophenyl)-1-naphthylamine] (III) (m.p. 204°C) was prepared by the nitration of trinitrophenyl-1-naphthylamine, which was obtained from 1-naphthylamine and chlorotrinitrobenzene. This new compound is soluble in NaOH ( $\approx 40$  mg per ml of 0.1 N NaOH); on the addition of K<sup>+</sup>, a dark-brown potassium salt is precipitated in a crystalline state. The solubility (40 mg per litre at 0°C) is much lower than that of II ( $\approx 0.3$  g per litre). For the quant. analysis of K the sample soln. is neutralised with 0.05 N NaOH and treated with a soln. of III (20 g per litre of 0.075 N NaOH) on a water bath and cooled with vigorous stirring. The ppt. is collected on a glass filter G4, washed with 0.01 N NaOH soln. saturated with III and water, and dried at 110°C. The presence of Na ( $< 25$  times the weight of the K), Mg ( $< 25$  times) and Ca ( $< 5$  times) does not give significant errors if care is taken. This method appears to be especially suitable for the determination of K in bitters.

K. SAITO

**3291. A colorimetric method for the determination of copper in alloyed steels with 2:2'-diquinolyl.** W. T. Elwell (*Analyst*, 1955, **80**, 508-514).—A colorimetric procedure is recommended for the determination of Cu in many metals and alloys,

including plain-carbon and high-alloyed steel, ferro-alloys (with W, Mo, Va and Ti), pure Co and pure Ni containing 0.001 to 1 per cent. of Cu. Steel (0.5 g) is dissolved in conc. HCl and HNO<sub>3</sub> and the soln. is evaporated just to dryness, the evaporation being repeated after addition of a little HCl. The residue, dissolved in dil. HCl, is treated with H<sub>2</sub>SO<sub>4</sub>, boiled, treated with citric acid soln. and diluted to 100 ml. A 10-ml aliquot is adjusted to between pH 5 and 6 with aq. NH<sub>3</sub> and 2 ml of 5 per cent. sodium acetate soln. are added. The vol. is adjusted to 17.5 ml and the soln. is extracted with 10 ml of a soln. of 50 mg of 2:2'-diquinolyl in 100 ml of pentanol. The optical density of the filtered extract is measured at 546 m $\mu$  at 20° C against a blank soln. ( $E_{1\text{cm}} \times 0.109 \equiv \text{mg of Cu}$ ), or with a Spekker absorptometer with Calorex H503 and Ilford No. 604 filters. The violet colour is stable. Modifications for samples other than steel are described.

A. O. JONES

**3292. Flame-spectrophotometric determination of copper in non-ferrous alloys.** J. A. Dean (*Anal. Chem.*, 1955, **27** [8], 1224-1229).—Rapid determinations of  $\geq 5$  per cent. of copper in Al-, Sn- and Zn-base alloys can be made with the Beckman DU flame spectrophotometer using the copper-arc emission lines (oxy-acetylene flame) at 324.7 m $\mu$  (for Cu concn.  $< 100$  p.p.m.) or 327.4 m $\mu$  (for Cu concn.  $> 100$  p.p.m.). The 324.7 line is the more sensitive but is subject to strong self-absorption. Only Ni in appreciable amounts ( $> 2000$  p.p.m.) interferes, but Sn, Sb and As should be removed initially by volatilisation of the bromides. The method is sensitive to  $\approx 1$  p.p.m. per scale-division and the standard deviations are within  $\pm 3$  per cent. An analysis takes only a few min. following dissolution of the sample (1 to 15 mg) in 6 N HClO<sub>4</sub> or 8 N HNO<sub>3</sub>. It is unnecessary to include silver as an internal standard since the usual (peak-luminosity minus background) values are accurate.

W. J. BAKER

**3293. Spectrophotometric determination of copper with salicylaldoxime. Application to analysis of aluminium alloys.** S. H. Simonsen and H. M. Burnett (*Anal. Chem.*, 1955, **27** [8], 1336-1339).—The rapid spectrophotometric determination of  $\geq 7$  per cent. of Cu in alloys of Al and Zn depends on the formation of cupric salicylaldoximate, which is extracted quantitatively into *n*-amyl acetate from a well-buffered aq. soln. at a pH of  $\approx 4.4$ , interference by other elements being negligible at this pH. The soln. of the sample (0.1 g) is made up to 250 ml, of which 25 ml are diluted to 100 ml with 50 ml of NaOH-potassium phthalate buffer and 25 ml of water. An aliquot (10 ml) of this soln. is extracted with 10 ml of a 0.02 M soln. of salicylaldoxime in *n*-amyl acetate. After 15 min. the extracted phase is transferred to an absorption cell and the transmittance is measured at 344 m $\mu$  against a blank. The range of max. photometric accuracy is 2.5 to  $8.5 \times 10^{-3}$  moles of Cu per litre of the extracted phase. The mean error is within 0.04 per cent.

W. J. BAKER

**3294. Micro-volumetric determination of silver and copper in coinage.** A. M. Amin (*Chemist Analyst*, 1955, **44** [1], 17-19).—The sample (4 to 5 mg) is dissolved in 1 ml of conc. HNO<sub>3</sub>, and 5 ml of water are added. The solution is evaporated almost to dryness, the residue is dissolved in water, and the solution is made up to 25 ml. Buffer solution (NH<sub>4</sub>Cl-aq. NH<sub>3</sub>) is added to 5 ml of this solution until the ppt. which first forms is

redissolved, and the soln. is ammoniacal. Murexide indicator (0.2 to 0.4 mg) is added and the solution, if not yellow, is diluted with water to obtain the yellow colour. The solution is then titrated with standard EDTA (disodium salt) solution until a permanent purple-red colour is obtained; the volume of EDTA required is equivalent to the copper in the sample. Potassium nickel tetra-cyanide (4 mg) is then added to the solution, and the original yellow colour returns. The volume of EDTA now required to give a permanent purple-red colour is equivalent to the silver in the sample.

D. LIFF

**3295. Determination of silver in refined bismuth.** D. Nordling (*Chemist Analyst*, **44** [1], 24).—The sample (15 g) is dissolved in 100 ml of conc. HNO<sub>3</sub>, and, after boiling to expel acid fumes, 30 g of EDTA (disodium salt) are added. Conc. aq. NH<sub>3</sub> (30 ml) is added and the solution is filtered. The alkaline filtrate is diluted to 300 ml, and 10 ml of 1:2:3-benzotriazole solution (2.5 g in 30 ml of conc. aq. NH<sub>3</sub>, diluted to 100 ml with water) are added and the mixture is digested for 30 min. at 80° C. The hot solution is filtered, and after being washed with hot water the ppt. is dried for 1 to 2 hr. at 100° C; wt. of ppt.  $\times 0.4774 = \text{wt. of silver present}$  (cf. Cheng, *Anal. Abstr.*, 1954, **1**, 2347).

D. LIFF

**3296. Complex citrates of metals in inorganic analysis. I. Some preliminary observations and the application of citrate complex formation in the qualitative analysis of the metal ions of the silver group.** A. K. Mukherji, A. K. Sinha and A. K. Dey (*Anal. Chim. Acta*, 1955, **12** [6], 501-503).—When aq. Na citrate is added to a soln. of a Ag<sup>+</sup>, Hg<sup>+</sup> or Pb<sup>+</sup> salt the ppt. which is first formed dissolves in an excess of citrate. Lead chloride is readily sol. in aq. Na citrate, but AgCl and HgCl are insol., and this difference can be used in the separation of the group 1 metals. Lead sulphate is also sol. in aq. Na citrate and can thus be separated from BaSO<sub>4</sub> and SrSO<sub>4</sub>, which are insoluble.

W. C. JOHNSON

**3297. Solvent extraction in the analysis of the precious metals.** W. A. E. McBryde (*Analyst*, 1955, **80**, 503-508).—Present-day applications of solvent extraction for the analytical separation of gold and the six metals of the platinum group are summarised. Solvent extraction of the halogen complexes, oxides, complexes with SnCl<sub>2</sub> and organic complexes are discussed. In the selection of an extraction method, consideration must be given to the composition of the mixture of metals to be analysed and to the subsequent treatment of the sample. The extraction of the metals themselves from reducing fluxes into collecting buttons (e.g., with lead) is also discussed.

A. O. JONES

**3298. Determination of magnesium by means of Titan yellow.** P. Schachtschabel and H. Isermeyer (*Z. Pflernähr. Düng.*, 1954, **67** [1], 1-8).—Magnesium is determined colorimetrically by using the red adsorption compound formed between colloidal Mg(OH)<sub>2</sub> and Titan yellow in alkaline solution. Max. extinction differences between Mg and the blank solutions occur at 545 to 550 m $\mu$ , linear calibrations being given by 5 or 10 ml of 0.05 per cent. Titan yellow with 0.02 to 0.15 mg or 0.02 to 0.30 mg of Mg, respectively. The best protective colloid is 2 per cent. poly(vinyl alcohol) ("poly-viol") and 10 per cent. glycerol, i.e., 20 g of "poly-viol" dissolved in 100 ml of warm glycerol and

diluted to colour in (5 ml of Titan yellow solutions of concn. of extinction to each 2 of 2 N cent., which free glass mental co

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diluted to 1000 ml with hot water. Constant colour intensity is maintained after 30 to 90 min. (5 ml of Titan yellow) or 40 to 90 min. (10 ml of Titan yellow). The "polyviol" and Titan yellow solutions are stable for up to 3 months. Calcium concn. of 5 mg per 50 ml cause max. increases in extinction; thus 10 ml of 0.025 N  $\text{CaCl}_2$  are added to each 20 ml of magnesium test solution and 5 ml of 2 N NaOH. The overall accuracy is  $\pm 6$  per cent., which may be improved by using magnesium-free glass apparatus and filters and, uniform experimental conditions for addition of the Titan yellow.

D. R. GLASSON

**3299. Spectrographic determination of magnesium in limestone.** L. V. Drutskaya and I. L. Reznikov (*Zavod. Lab.*, 1955, **21** [3], 324-327).—The powdered sample in the hollowed-out end of a carbon electrode is sparked, and the lines Ca 3007 Å and Mg 3097 Å are measured. Contents of 0.5 to 5 per cent. of MgO in limestone can be determined.

G. S. SMITH

**3300. Amperometric titration of calcium with the disodium salt of ethylenediaminetetra-acetic acid.** R. F. Sympton (*Dissert. Abstr.*, 1955, **15** [1], 36, Publ. No. 10,552).—An amperometric titration method developed for determining Ca involves reaction between Ca and EDTA (disodium salt) with zincate ion in KOH as the indicator ion, and measurement of the decrease in diffusion current of the zincate after completion of the Ca-EDTA reaction. When titrating 3 to 11 mg of Ca in an initial vol. of 50 ml the deviation was 0.59 per cent., but with samples  $> 2$  mg (initial concn.  $< 0.001$  M Ca) results were low. In moderate amounts Mg did not interfere. The method compares favourably in accuracy with other volumetric methods and is more accurate but less sensitive than optical methods.

L. F. TAYLOR

**3301. Sources of error in the flame-photometric determination of calcium, and their elimination.** K. Scharrer and J. Jung (*Z. Pflernähr. Düng.*, 1954, **67** [3], 240-248).—The type and magnitude of errors in the flame-photometric determination of Ca are investigated by using a Zeiss flame photometer (model III) with a "Zeiss 56" calcium filter and an acetylene and compressed-air flame. Depressions in the emission of Ca caused by the addition of known amounts of  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are recorded, the calibration curves obtained under these conditions enabling more accurate and reproducible values to be obtained for solutions containing these ions.

D. R. GLASSON

**3302. The chromatographic separation of a mixture of the chlorides of calcium, strontium, barium and magnesium.** T. Barnabas, M. G. Badve and J. Barnabas (*Anal. Chim. Acta*, 1955, **12** [6], 542-543).—The method of Giri and Rao (*J. Ind. Inst. Sci.*, 1952, **34**, 95) is used for the separation of the chlorides of Ca, Sr, Ba and Mg, mixtures of methanol with ethanol (1 + 1), isopropanol (3 + 2), butanol (7 + 3), and pentanol (7 + 3) being used as solvents. The dried chromatograms are sprayed with a filtered soln. of 2:6-dichlorophenolindophenol (0.2 g) and  $\text{AgNO}_3$  (3 g) in ethanol (100 ml). The following are the  $R_F$  values obtained when a mixture of methanol and ethanol (1 + 1) is used—Ca, 0.62; Sr, 0.49; Ba, 0.28; Mg, 0.80.

W. C. JOHNSON

**3303. Barite analysis with X-ray spectrograph.** L. B. Gulbransen (*Anal. Chem.*, 1955, **27** [7], 1181-1182).—Quant. determination of Ba in barite

ores ( $-400$  mesh) can be effected in  $\approx 3$  min. with the X-ray spectrograph (tungsten target, NaCl analysing crystal) using the  $\text{BaL}_{\beta_1}$   $54.16^\circ$  ( $2\theta$ ) line, a scale factor of 32 and a Geiger tube operated at 1500V. A standard calibration curve for the range 25-6 to 100 per cent. of  $\text{BaSO}_4$  is established, no background correction being necessary. The results are within 0.2 to 0.5 per cent. ( $\text{BaSO}_4$ ) of those obtained by the usual gravimetric method.

W. J. BAKER

**3304. Analytical determination of radium.** O. Gübeli and H. Jucker (*Helv. Chim. Acta*, 1955, **38** [2], 485-491).—Emanometric determinations of Ra agree well with direct radiation-counter measurements on solid preparations. In the analytical method developed, inactive  $\text{BaSO}_4$  is added to the radium salts so as to give a constant testing thickness of 8 mg per sq. cm (calculation factors are also given for other thicknesses). The Ra is quant. separated by  $\text{BaSO}_4$  of optimum particle size. This is attained when the Ra solution in 0.1 N  $\text{H}_2\text{SO}_4$  is buffered at pH 3, heated on a water bath and treated with a slight excess of 0.1 M  $\text{BaCl}_2$ , introduced dropwise from a micro-burette. Anions such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$  and acetate do not interfere. Radioactive equilibrium is established in  $< 40$  days. Amounts of 0.0001  $\mu\text{g}$  and 0.001  $\mu\text{g}$  of Ra in 100 ml of solution are determined with accuracies of  $\pm 3$  per cent. and  $\pm 1$  per cent. A rapid method in which radioactive equilibrium is not established affords 2 per cent. accuracy for amounts of 0.01 to 0.5  $\mu\text{g}$  of Ra per 100 ml.

D. R. GLASSON

**3305. The direct determination of combined oxygen in metals and metal oxides. I. The determination of zinc oxide in zinc dust and zinc ash.** E. Eberius and W. Kowalski (*Erzmetall*, 1954, **7** [6], 229-234).—Methods for determining ZnO in zinc dust and ash are critically reviewed. A new and rapid method is described in which the test material is treated with anhydrous hydrogen halides, e.g., HBr in toluene-ether, or HCl in acetic acid, the water formed by reaction with the ZnO being determined by Karl Fischer solution. The best procedure consists in dissolving samples of ZnO (0.2 to 0.5 g) or zinc dust (2 to 5 g, dried at  $110^\circ\text{C}$ ) in acetic acid (30 ml) saturated with HCl ( $\approx 2.5$  moles per litre), using Erlenmeyer narrow-necked flasks (100 to 300 ml) and, if necessary, temp. up to  $60^\circ\text{C}$ . Addition of anhydrous pyridine (20 ml per g of test material) neutralises the excess of HCl and keeps the pyridinium chloride in solution. Titration with Karl Fischer solution and comparison with a blank determination affords an accuracy of  $\pm 0.8$  per cent. for ZnO and  $\pm 0.6$  per cent. for zinc-dust samples.

D. R. GLASSON

**3306. Volumetric determination of mercury and the use of mercury salts as primary acidimetric standards.** S. R. Palit and G. R. Somayajulu (*Anal. Chem.*, 1955, **27** [8], 1331-1333).—In the procedures described, the  $\text{Hg}^{II}$  salt (0.1 millimole of Hg in 20 ml of soln.) is converted into  $\text{HgO}$ , which is kept in soln. by complexing with acetamide ( $\approx 70$  mg) or urea (4 to 5 g). The soln. is made alkaline with a slight excess of dil. NaOH soln. and neutralised (phenolphthalein indicator) by dropwise addition of 0.1 N  $\text{HClO}_4$  or  $\text{HNO}_3$ . About 12 ml of 0.5 N aq. KI (or excess of aq.  $\text{Na}_2\text{S}_2\text{O}_3$ ) are then added and the titrated NaOH is titrated with 0.1 N HCl (phenolphthalein indicator). Interfering ions are  $\text{Cl}^-$ ,  $\text{SCN}^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CN}^-$  and  $\text{PO}_4^{3-}$ ; in the presence of  $\text{Cl}^-$  a very sharp end-point is assured by conducting the first neutralisation with alcoholic NaOH

in 75 per cent. ethanol;  $\text{PO}_4^{'''}$  can be removed by neutralising with  $\text{Ba}(\text{OH})_2$  instead of  $\text{NaOH}$  and treating the filtrate as usual. The general procedure can also be applied to  $\text{Hg}^{\text{I}}$  salts because  $\text{Hg}^{\text{I}}$  is converted quant. into  $\text{Hg} + \text{Hg}^{\text{II}}$  when  $\text{NaOH}$  is added to the soln. in the presence of an amide. The ppt. of mercury is filtered off and washed, the  $\text{Hg}^{\text{II}}$  in the filtrate being determined volumetrically by the above method. The error is within  $\pm 0.2$  per cent. so that pure mercury salts can be used for standardising both weak and strong alkalis and acids by adopting either the first or second stage of the procedure described above. W. J. BAKER

**3307. The heterometric determination of mercury or mercaptobenzothiazole.** M. Bobtelsky and E. Jungreis (*Anal. Chim. Acta*, 1955, **12** [6], 562-571).—The heterometric method (*Anal. Abstr.*, 1954, **1**, 1770) is applied to the determination of  $\text{Hg}^{\text{II}}$  with mercaptobenzothiazole (I) and of I with  $\text{Hg}^{\text{II}}$ . The titration of  $\text{Hg}^{\text{II}}$  is possible in the pH range 2 to 10, but is preferably carried out in acid soln., as follows. To 20 ml of aq.  $\text{Hg}(\text{NO}_3)_2$ , containing 1 to 2 mg of  $\text{Hg}^{\text{II}}$ , add 1 ml of *M* acetic acid and titrate with alcoholic 0.005 *M* or 0.01 *M* I. One mole of  $\text{Hg}$  is precipitated by 2 moles of I. In more strongly acid solutions, alcohol ( $> 50$  per cent.) must be added to ensure a good end-point. In the alkaline titration the original soln. must contain 25 to 50 per cent. of alcohol, and 1 ml of *M* Na acetate is added, or alternatively 1 ml of 2 *N*  $\text{NH}_4\text{NO}_3$  and 1 ml of 0.2 *N*  $\text{NaOH}$ . The titration shows a sharp max. since the ppt. dissolves in an excess of I. The max. error in acid or alkaline soln. is 3 per cent. Ethylenediaminetetra-acetic acid does not interfere with titrations in aq. acetic acid or acetate soln. In the presence of Na citrate or tartrate the titration is performed in dil. alcoholic soln. Similarly an alcoholic soln. (20 to 25 per cent.) (20 to 30 ml) of I (1 to 2 mg) can be titrated with 0.001 to 0.003 *M*  $\text{Hg}(\text{NO}_3)_2$ . W. C. JOHNSON

**3308. Heterometric micro-determination of mercury with mercaptobenzothiazole in the presence of an excess of foreign metals.** M. Bobtelsky and E. Jungreis (*Anal. Chim. Acta*, 1955, **13** [1], 72-78).—Microgram amounts of  $\text{Hg}$  can be titrated heterometrically in the presence of an excess of many metals without the use of a complexing agent. The max. concn. for Ca, Ba, Mg, Zn, Mn, Ni, Co and Cd is 0.2 *M*, for Pb  $< 0.1$  *M*, and for Al, Cr and Fe  $< 0.05$  *M*. The titration occupies 20 to 30 min. and gives an error of  $< \pm 3$  per cent. Interference due to an excess of Bi can be removed in acetic acid or sodium acetate soln. by the addition of EDTA (tetrasodium salt), and that due to an excess of Cu by the same reagent in acetic acid soln. only. The addition of sodium citrate in alkaline soln. will also remove the interference of Cu. J. H. WATON

**3309. Determination of 202-labelled mercury and other mercury isotopes in samples of mercury vapour by mercury resonance radiation absorptiometry.** K. R. Osborn and H. E. Gunning (*J. Opt. Soc. Amer.*, 1955, **45** [7], 552-555).—The proportion of  $^{202}\text{Hg}$  present in small samples, only a few  $\mu\text{g}$ , can be determined by a method which depends on measuring the absorption of the  $^{202}\text{Hg}$  component of the resonance radiation of  $\lambda = 2537 \text{ \AA}$ . The source of this radiation is an electrodeless discharge lamp containing a drop of  $\text{Hg}$  (98.3 atoms per cent. of  $^{202}\text{Hg}$ ) and a few mm pressure of argon. The detector is a tantalum cathode photocell, Westing-

house type WL775. Samples to be analysed are introduced into a thermostatically controlled fused-silica cell in the optical path and the absorption is measured. Over a wide range of  $^{202}\text{Hg}$  concentration, results agree with values obtained by mass spectrometry within 2 per cent. The method requires very much smaller samples than the mass spectrometer, and contamination from earlier samples introduced is avoided. B. S. COOPER

**3310. The separation of mercury from gold by ion exchange.** W. M. MacNevin and I. L. Lee (*Anal. Chim. Acta*, 1955, **12** [6], 544-546).—Small quantities of  $\text{Hg}^{\text{II}}$  (8 g) are separated from comparatively large quantities of  $\text{Au}^{\text{III}}$  (400 g) by passing a soln. of their chlorides in 2 *N*  $\text{HCl}$  (1800 ml) through a column of Dowex 50 cation-exchange resin (800 g). The  $\text{Hg}^{\text{II}}$  behaves as a cation and is retained by the resin; the Au passes through as the anion,  $\text{AuCl}_4^-$ , and the column is finally washed with water until the eluent is no longer yellow. W. C. JOHNSON

**3311. Determination of decaborane.** W. H. Hill and M. S. Johnston (*Anal. Chem.*, 1955, **27** [8], 1300-1305).—A direct micro-determination of decaborane can be made either by measuring the strong u.v. absorption at 265 to 270  $m\mu$  of its soln. in aq. triethanolamine (1 + 1), or colorimetrically by measuring the absorption at 490  $m\mu$  of the sol. red addition product of decaborane with quinoline (2 per cent. v/v) in the presence of xylene. Beer's law is valid for both methods, and from 1 to 25  $\mu\text{g}$  of boron per ml can be determined accurately. The first method, which is unaffected by the very slow hydrolysis of decaborane in the solvent, can be applied to the dynamic and static analysis of air and gases containing  $\text{B}_{10}\text{H}_{14}$ . The air or vapour is bubbled slowly through two glass bulbs containing aq. triethanolamine, the contents are afterwards combined, diluted conveniently and the u.v. absorption is determined ( $\text{B}_{10}\text{H}_{14}$  recovery is  $\approx 98$  per cent.). Static-air samples are taken with a gas-pipette (250 ml) into which 5 ml of the triethanolamine soln. are introduced. In the colorimetric method, which is generally preferred, the spectrophotometric readings should be taken  $\approx 1\frac{1}{2}$  hr. after mixing the solutions; the colour is extremely stable, and the concn. of decaborane is obtained by reference to prepared standardisation curves. This method is very efficient and accurate for dynamic-air analyses, only one absorption bulb (containing 2 per cent. of quinoline in xylene) being needed. Interference by diborane and pentaborane is negligible in both methods, provided the standard procedures are followed. W. J. BAKER

**3312. Modification of Schwarz von Bergkampff's method for determining aluminium.** H. Shehyn (*Anal. Chem.*, 1955, **27** [8], 1341).—In applying the method of Schwarz von Bergkampff (*Z. anal. Chem.*, 1931, **83**, 345) to high-Fe ferro-aluminium alloys, the removal of Fe as sulphide is replaced by electrolysis on a mercury cathode. Whilst the cupferron pptn. of titanium from acid soln. is unaffected, oxidation of the excess of cupferron during subsequent warming of the ammoniacal soln. causes contamination of, and difficulty in filtering, the ppt. of Al oxinate. Addition of 5 ml of tartaric acid (100 g per litre) and 1 ml of 65 per cent. aq. hydrazine hydrate before making the soln. ammoniacal eliminates the trouble completely, and the pptn. of Al with 5 per cent. oxine soln. can then be made by the usual procedure. W. J. BAKER

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**3313. Analysis of high-purity aluminium with special reference to requirements in practice.** F. E. Faller (*Erzmetall*, 1954, 7 [11], 473-479).—Spectrographic, polarographic, photometric, gravimetric and volumetric methods for analysing purified Al are reviewed. In developing newer methods, the working time is reduced by more rapid dissolution of the test materials when they are more finely divided and are treated with either 25 to 30 per cent. NaOH soln. or with HCl containing  $\text{HgCl}_2$  as an accelerator. For the determination of single elements, the extinction curves are shown for Cu as diethyldithiocarbamate in  $\text{CCl}_4$ , Fe as *o*-phenanthroline, Si as molybdosilicate, Ni as the dimethylglyoxime complex, Zn as the dithizonate in  $\text{CCl}_4$ , and Ti as the sulphosalicylic acid complex. Copper may be determined to an accuracy of  $\pm 2$  p.p.m., after allowing for the extinction of the Ni diethyldithiocarbamate being 0.33 of that of Cu (for equal metal content) at 436 m $\mu$ . The accuracy of the remaining determinations is (in p.p.m.): Fe  $\pm 3$ , Si  $\pm 5$ , Ni  $\pm 2$ , Zn  $\pm 2$ , Ti  $\pm 1$ . Higher contents of Si must be determined gravimetrically as  $\text{SiO}_2$ . The EDTA method is recommended as the most rapid for determining Mg.

D. R. GLASSON

**3314. Determination of phosphorus in aluminium and aluminium oxide by radio-activation analysis.** L. M. Foster and C. D. Gaitanis (*Anal. Chem.*, 1955, 27 [8], 1342-1344).—The procedure described for determining 0.001 to 0.0001 per cent. of phosphorus in aluminium alloys and refined alumina involves irradiation of the sample (0.1 to 1 g) and of a standard ( $\approx 0.2$  g of  $\text{NH}_4\text{H}_2\text{PO}_4$ ) for one week in a slow neutron reactor, then adding 0.013 g of  $\text{NH}_4\text{H}_2\text{PO}_4$  as carrier, and separating the P as  $\text{Mg}_3\text{P}_2\text{O}_7$  by double pptn. with ammonium molybdate. The activities of the P thus separated from the sample and the standard are then compared under identical counting conditions ( $< 10,000$  counts, except for alloys very low in P where  $< 3000$  counts are taken). The results are accurate to within 5 per cent. for samples high in P and 10 per cent. for samples low in P; the method is sensitive to  $5 \times 10^{-7}$  per cent. of phosphorus. The error due to variation of flux over the containers is  $\approx 2$  per cent.; self-attenuation effects are absent in both sample and standard; other sources of error are discussed.

W. J. BAKER

**3315. Determination of the group of rare-earth metals.** L. Erdey, K. Kálmán and A. Almásy (*Acta Chim. Hung.*, 1955, 6 [1-2], 173-182).—A method has been developed for determining about 10 per cent. of rare-earth-metal oxides in the presence of 90 per cent. of  $\text{Ca}_3\text{PO}_4$ . One gram of material is dissolved in  $\text{HNO}_3$ , and the phosphate is pptd. with  $\text{NH}_4\text{MoO}_4$ . The suspension is made up to 500 ml and filtered, and 250 ml of the filtrate are treated with excess of aq.  $\text{NH}_3$  to ppt. the rare-earth hydroxides. The ppt. is collected on a 1G4 glass filter, washed, dissolved in HCl, evaporated, ignited, redissolved in 1 to 2 ml of HCl and 50 ml of water and pptd. hot with oxalic acid. After being heated for 30 min. and set aside for 12 hr. the ppt. is collected on a 1G4 glass filter and washed with aq. oxalic acid containing HCl. It is then redissolved in HCl and repptd. as above, filtered off and washed on a filter-paper, and ignited at 1000°C in a platinum crucible. The error is about 1 per cent. Cerium and Th are present as dioxides, Pr and Tb as oxides of varying composition, other metals as  $\text{R}_2\text{O}_3$ . Excess of oxygen above  $\text{R}_2\text{O}_3$  can be deter-

mined by the iodimetric method of Bunsen; for samples insoluble in HCl, the  $\text{CO}_2$  is generated from  $\text{KHCO}_3$  added to the aq. KI. A. B. DENSHAM

**3316. Rapid separation of tracer amounts of rare-earth elements of the yttrium group.** D. C. Stewart (*Anal. Chem.*, 1955, 27 [8], 1279-1282).—An effective separation of Tm, Tb, Lu, Er and Yb (e.g., in neutron-activation analysis) can be made within 30 min. by selective elution with 0.25 M aq. glycolic acid (buffered to pH 3.48 or 3.58) from cation-exchange resin columns  $< 1$  cm high and 2 mm in internal diam. The column-tubing is drawn down at the tip and the top is ground so as to be interchangeable with the burette containing the eluting soln. Control of resin size (preferably  $\sim 400$  mesh), drop size and flow rate are important; data are listed. The calcium in commercial glycolic acid must be removed initially by elution through a hydrogen resin (Dowex 50), and 0.05 per cent. of a wetting agent should then be added before adjusting the pH. Separation of Am from Cm and of Y from Tb is poor with these short columns.

W. J. BAKER

**3317. Thermogravimetric pyrolysis of cupferron complexes of scandium, yttrium and rare-earth elements.** W. W. Wendlandt (*Anal. Chem.*, 1955, 27 [8], 1277-1278).—Thermogravimetric analyses of the cupferrates of Sc, Y and rare-earths, pptd. quant. from soln. at pH 3 to 4, show that it is unnecessary to ignite the complexes to 900°C because the oxides are formed completely at 500° to 600°C. The anhyd. complexes of  $\text{Ce}^{IV}$  and Gd, in fact, begin to decompose at room temp. The construction and operation of a simple thermobalance are described.

W. J. BAKER

**3318. Compleximetric titrations (chelatology).** XIII. The determination of scandium. L. Wunsch (*Coll. Czech. Chem. Commun.*, 1955, 20 [5], 1107-1112).—Conditions for the direct and indirect compleximetric determination of Sc with EDTA (disodium salt), with Eriochrome black T as indicator, have been studied, and satisfactory results have been obtained. By masking with KCN and dimercaptopropanol, Sc can be determined in the presence of Zn, Cd, Ni, Co, Hg or Cu, or of small amounts of Pb, Bi or Fe. [This is a translation into German of a paper originally published in *Chem. Listy*, 1955, 49, 843.] N. E.

**3319. Carbon in steel: a review of physical methods of determination.** A. P. H. Jennings (*Iron & Steel*, 1955, 28 [6], 208-210).—Comparison of rapid physical methods which can be employed for differentiating between steels, particularly in relation to their carbon contents, indicates that those based on measurement of the magnetic properties of the sample are satisfactory and adequate, in general, for detecting differences of  $\pm 0.02$  per cent. of C. Some compensation for the effect of alloying elements is usually required and the metallurgical condition of the specimen must also be taken into account. The characteristics of various commercially available instruments are described.

J. O. LAY

**3320. Method of studying distribution of carbon in the cementation and decarburising of steel.** M. M. Zamyatnin, L. B. Getsov and E. L. Grinzald (*Zavod. Lab.*, 1955, 21 [3], 316-320).—Spectrographic determinations of carbon in steel at various distances below the surface are carried out by means of the lines C III 2296-89 Å and Fe III 2295-86 Å.

G. S. SMITH

**3321. Use of the continuous-current electric arc for quantitative analysis of silicates.** R. Ricard (*Mikrochim. Acta*, 1955, [2-3], 226-235).—The usual continuous arc between graphite electrodes provides a simple intense light source, sufficiently stable and reproducible for spectrographic methods of analysis. The emission spectra of silicates and, more generally, non-electrically conducting materials are registered during the first 15 sec. of the combustion. This procedure is justified by studies of distillation by the moving-plate method. The material being analysed (15 to 20 mg) must have been previously calcined to constant wt., i.e., it must not contain volatile products such as water of constitution. Nickel powder (980 mg) is added as a diluent to avoid saturation of the arc. The use of powdered graphite (1000 mg) and  $B_2O_3$  (5 mg) prevents globulation of the fused material and avoids contact with the sides of the crater (diameter 2 mm, depth 4 mm) in the graphite cathode; temp. differences are thus eliminated. A continuous current of 9 amp. is obtained from a 3-phase supply by using a copper oxide rectifier. Results are given for determinations of  $SiO_2$  in argillaceous materials, for concn. between 10 and 100 per cent. D. R. GLASSON

**3322. A rapid method for the determination of microgram quantities of germanium.** E. H. Strickland (*Analyst*, 1955, **80**, 548-551).—A rapid and accurate method for the determination of Ge in ores is presented. The sample is decomposed in hot conc.  $H_3PO_4$ , the residue is dissolved in conc. HCl and the Ge salt is extracted with  $CCl_4$ . From this soln. it is extracted with an ammonium oxalate-oxalic acid soln.,  $HNO_3$  is added and the soln. is evaporated just to dryness. The residue is subjected to one of two procedures. (a) The cold residue is dissolved in warm ammonium oxalate-oxalic acid soln., and 0.5 per cent. gelatin soln. is added, followed by a 0.1 per cent. soln. of quinalizarin acetate in methanol. After 30 min. the transmittance is determined at 500  $m\mu$ . (b) The residue is evaporated to dryness with  $NH_4SO_4$  then dissolved in this acid. Gelatin soln. is added, followed by a 0.05 per cent. soln. of phenylfluorone in ethanol. The transmittance is determined at 510  $m\mu$  after 30 min. A calibration graph is constructed from solutions of  $GeO_2$  in ammonium oxalate-oxalic acid, which are evaporated with  $HNO_3$  and treated according to procedure (a) or (b). In the presence of substantial amounts of  $Cl^-$ , the method of decomposition needs modification as loss of Ge as  $GeCl_4$  occurs. A. O. JONES

**3323. The absorptiometric determination of tin by means of dithiol.** T. C. J. Ovenston and C. Kenyon (*Analyst*, 1955, **80**, 566-567).—It was previously reported (Kenyon *et al.*, *Brit. Abstr. C*, 1952, 137) that certain dispersants can be used to permit normal absorptiometric techniques to be applied to the determination of small amounts of Sn, by Clark's method, with dithiol (*Brit. Chem. Abstr. A*, 1936, 696; *AI*, 1937, 581). Of a number of dispersants investigated, Lorol (sodium lauryl sulphate) proved most satisfactory and, unlike some other dispersants, may be added before the dithiol, thus producing a less turbid liquid. The tin-dithiol complex in the presence of Lorol has an absorption max. at 533  $m\mu$  measured against a reagent blank. The specific extinction coeff. at this wavelength is 0.061 per cm per p.p.m. of Sn. A. O. JONES

**3324. Voltammetry at constant current. Application to lead ion in nitric acid solution.** M. M. Nicholson and J. H. Karchmer (*Anal. Chem.*, 1955, **27** [7], 1095-1098).—A const.-current electrolysis cell (with built-in  $HgCl_2$  electrode and removable auxiliary electrode), current- and voltage-measuring circuits, and a rapid-response electronic strip-chart recorder are described and their combined use for the const.-current voltammetry of  $Pb^{++}$  in aq. 0.02  $M$   $HNO_3$  is explained fully. Potential-time curves for various concn. and electrode areas are shown. The procedure is applicable to the quant. analysis of electro-reducible and electro-oxidisable substances, and to determinations of composition and thickness of films on metal surfaces, because the precision is equiv. to a total deviation of  $\pm 1$  per cent. in  $Pb^{++}$  for concn. between 0.0002 and 0.02 mole per litre. Moreover, the electrodes can be stationary rather than dropping or rotatory. Although  $\approx 40$  per cent. of the lead was present as the mono-nitrate complex in the cell solutions, no kinetic effect on the electrolysis was observed.

W. J. BAKER

**3325. Determination of several impurities contained in lead and in lead-tin alloys.** G. Delassus (*Chim. Anal.*, 1955, **37** [7], 241-242).—The determination of Cu, Cd and Zn in Pb and Pb-Sn alloys is effected polarographically after pptn. of Pb as  $PbSO_4$  and separation from Sn with  $Na_2S$ . *Procedure*—Dissolve 0.5 to 0.8 g of sample in 10 ml of a 10 per cent. soln. of Br in HBr. Carefully bring the soln. to boiling point and then allow digestion for 2 min. at a moderate temp. Remove the Pb by fuming with 5 ml of conc.  $H_2SO_4$ , diluting, boiling, cooling and filtering off the ppt. Neutralise the filtrate with conc. NaOH soln. and add 25 ml of a 50 per cent. soln. of  $Na_2S$ . Boil, then allow to stand, and filter off the sulphides of Cu, Cd and Zn; the Sn remains in the filtrate. Treat the filter and residue with the min. of  $HNO_3$  and filter off the paper pulp. Boil the soln., cool and adjust to pH 7 with NaOH soln. Pour into a 150-ml calibrated flask, and add 25 ml of 12  $N$  aq.  $NH_3$  soln., 10 g of  $NH_4Cl$ , 2 ml of a saturated  $Na_2SO_3$  soln. and 1 ml of a freshly prepared 2 per cent. soln. of Tylose. Make up to 150 ml and the soln. is then ready for the polarographic estimation of Cu, Cd and Zn. The half-wave potentials under these conditions are -0.24 and -0.50 V for Cu, -0.81 V for Cd and -1.43 V for Zn. The simultaneous determination of  $< 0.001$  per cent. of each element is possible with an error of  $\approx \pm 1$  per cent. J. H. WATON

**3326. Identification of rutile and anatase titanium dioxide by means of the Zeiss spectrophotometer.** A. J. van Joest (*Verhroniek*, 1955, **28** [7], 195-196).—Reflectance curves are given for various commercial samples of these two pigments in methylcellulose and in alkyl media, and for mixtures of the two types in methylcellulose over the range 370 to 420  $m\mu$ . In spite of the scatter of figures between different samples, the distinction between them is clear; e.g., in methylcellulose, rutile samples have reflectances in the range 8 to 11 per cent. at 370  $m\mu$  and anatase samples in the range 25 to 32 per cent. Mixtures have intermediate values. D. R. DUNCAN

**3327. The rapid estimation of titanium in alloy steel.** W. F. Pickering (*Anal. Chim. Acta*, 1955, **12** [6], 572-576).—The proposed method is applied to the analysis of stainless steel containing  $\approx 18$  per cent. of Cr,  $\approx 10$  per cent. of Ni and  $\approx 0.5$  per cent. of Ti. *Procedure*—Dissolve 0.25 g of steel in

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20 ml of 5 N HCl and 5 ml of conc.  $\text{HClO}_4$  and evaporate to strong fumes of  $\text{HClO}_4$ . Dissolve the residue in 40 ml of "Vermag" reagent (prepared by dissolving 37.5 g of EDTA in 5 N NaOH to give a soln. just acid to phenolphthalein, adding 50 g of magnesium sulphate and diluting to 1 litre) and the soln. strongly ammoniacal with 5 N aq.  $\text{NH}_3$  soln., agitate vigorously and set aside for several min. Filter through a Buchner funnel and wash the ppt. with water. Dissolve the ppt. in 250 ml of 5 per cent. aq.  $\text{H}_2\text{SO}_4$ , add aq.  $\text{H}_2\text{O}_2$ , and determine the transmittancy at 425 m $\mu$ . Prepare a calibration graph with known quantities of Ti. The EDTA sequesters interfering metals and the  $\text{MgSO}_4$  provides a "carrier" for the pptn. of the Ti. Adsorption of  $\text{CrO}_4^{2-}$  on the ppt. is a source of error. Results are obtained in 30 min. and are accurate within  $\pm 5$  per cent. W. C. JOHNSON

**3328. Determination of traces of certain rare earths in zirconium.** H. J. Hettel and V. A. Fassel (*Anal. Chem.*, 1955, **27** [8], 1311-1314).—A procedure for the determination of  $< 2$  p.p.m. each of Gd, Tb, Dy, Ho and Sm in zirconium for nuclear reactors is described fully. The sample (100 g) is treated with aq. HF and the cool, dil. soln. (to which are added 20 mg of pure  $\text{Y}_2\text{O}_3$  in dil. HCl) is passed through a cation-exchange column (36 in.  $\times$  1 in., Dowex-50 resin, 50 to 60 mesh) on which the rare-earth cations and the  $\text{Y}_2\text{O}_3$  carrier are retained, whilst  $\text{ZrF}_6^{2-}$  remain in the eluate. After elution of the column with 6 N HCl, the concentrated rare earths plus carrier are separated from other cationic impurities in the sample by standard chemical methods, and are then determined spectrographically in the  $\text{Y}_2\text{O}_3$  carrier by the method of Fassel *et al.* (*Anal. Abstr.*, 1955, **2**, 3000; *Spectrochim. Acta*, 1952, **5**, 201). Recoveries are quant. to within 10 per cent.; the sources of experimental error, mainly spectroscopic, are discussed. The general procedure is applicable to the determination of these five rare earths in any element that dissolves in HF to form a stable anionic complex (Be, Si, B, Ge, Ti, etc.). W. J. BAKER

**3329. Chemistry of thorium. II. Volumetric determination of thorium.** N. K. Dutt and A. K. Chowdhury (*Anal. Chim. Acta*, 1955, **12** [6], 515-518).—Thorium is precipitated with *m*-nitrobenzoic acid according to the established gravimetric procedure and the *m*-nitrobenzoate is washed with a 5 per cent. soln. of the acid, and then with ethanol until free from acid. The ppt. is then dissolved in 25 ml of 40 per cent.  $\text{H}_2\text{SO}_4$  and 25 ml of water and the nitro group is titrated with standard  $\text{TiCl}_3$  by the procedure of English (*Ind. Eng. Chem.*, 1920, **12**, 994). W. C. JOHNSON

**3330. Determination of thorium with organic reagents: different methods using 4-aminosalicylic acid.** S. K. Datta and G. Banerjee (*Anal. Chim. Acta*, 1955, **13** [1], 23-27).—Thorium is quant. pptd. at pH 4 to 5.6 by a hot 2 per cent. soln. of 4-aminosalicylic acid in the presence of a little ammonium acetate. The composition of the ppt. is  $(\text{C}_7\text{H}_6\text{O}_5\text{N})\text{Th}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ , with some slight variation in the no. of  $\text{H}_2\text{O}$  mol. The Th can then be determined gravimetrically by ignition to  $\text{ThO}_2$ . Alternatively, the aromatic nuclei can be quant. halogenated with a bromide-bromate mixture or with  $\text{ICl}$ . The results from the three methods are comparable and agree well with the amounts of Th taken. J. H. WATON

**3331. Estimation of thorium by organic reagents. VII. Separation from cerite earths and other metals by 4-aminosalicylic acid.** S. K. Datta and G. Banerjee (*J. Indian Chem. Soc.*, 1955, **32** [4], 231-233).—Methods are described for separating Th from cerite earths and a number of common elements by 4-aminosalicylic acid. Single pptn. is used for solutions having a thoria-cerite earth oxide ratio of 1:13; for ratios above this, up to 1:23, double pptn. is necessary. A pH of 4 to 5.6 is suitable. Thorium can also be separated from monazite sand after neutralising to Congo red and adding a little ammonium acetate. Metals such as U, Al, Cr, Ni, Co, Mn, Zn, Ca, Sr, Ba and Mg in moderate amounts do not interfere with the estimations; metals such as Fe, Zr and Ti interfere and are co-pptd. with Th; and metals such as Ag, Hg, Pb and Sn are also pptd. by 4-aminosalicylic acid. O. M. WHITTON

**3332. Determination of nitrogen [in steel] by the distillation method.** B. A. Generozov (*Zavod. Lab.*, 1955, **21** [3], 302-303).—A very rapid transfer of  $\text{NH}_3$  from the distillation vessel containing the ammonium salt and NaOH to the absorption vessel is attained by suction, which draws air through the liquid being distilled. The absorption vessel contains water containing methyl red-methylene blue mixed indicator and carries a burette filled with 0.01 N acid, for titration of the  $\text{NH}_3$  absorbed at intervals during the distillation. To determine N in steel, 1 g (for contents of N  $< 0.2$  per cent.) or 0.5 g (for higher contents) is dissolved in dil. HCl (1 + 1) unless the steel contains stable nitrides, when the method of decomposition described earlier (*Ibid.*, 1947, **13**, 314) is used. A soln. of 40 per cent. NaOH (60 to 70 ml) is added, 25 to 30 ml of water containing the indicator are placed in the absorption vessel, the NaOH solution is heated and air is sucked through at the rate of 3 litres per min. Whenever the absorption solution turns green it is titrated with acid to give a red colour. Distillation is stopped when the red colour of the distillate remains unchanged for 1 to 2 min. G. S. SMITH

**3333. Micro-determination of phosphorus.** D. N. Rhodes (*Nature*, 1955, **176**, 215-216).—The method of Allen (*Biochem. J.*, 1940, **34**, 858) for determining inorganic phosphate in turbid or coloured solutions has been used for simplifying the method for determining total phosphorus and for increasing its sensitivity about ten-fold. After digestion of the sample with  $\text{HClO}_4$ , the colour is developed in the digestion flask as described by Allen and, after 5 min., 3 ml of isobutyl methyl ketone are added and the flask is shaken for 1 min. To facilitate the removal of the ketone layer, the contents of the flask are poured into a test-tube (diameter 0.5 in.), or the interface is brought into the neck of the digestion flask by the addition of water saturated with the ketone. The ketone layer is transferred by pipette to a 1-cm cuvette and the extinction at 680 m $\mu$  is measured. The blue colour fades slightly during the first 30 min. after extraction, but then remains constant for at least 1 hr. As little as 1  $\mu$ g of phosphorus can be estimated. K. A. PROCTOR

**3334. Separation of small amounts of phosphoric acid from iron and vanadium by extraction and ion exchange.** W. Fischer, R. Paul and H.-J. Abendroth (*Anal. Chim. Acta*, 1955, **13** [1], 38-45).—In the presence of excess of  $\text{MoVI}$ , P is extracted with ethyl acetate at acidities  $< 1.2$  N as acid sodium dodecamolybdophosphate. For acidities  $> 2$  N,

the extraction of P diminishes, since more Mo is removed as molybdenyl compounds. The presence of  $V^{IV}$  and  $Fe^{III}$  causes no interference at acidities from 1.2 to 1.5 N, but  $V^V$  and  $Fe^{II}$  interfere seriously. A cation-exchange resin, such as Lewatit KS 22, will separate P from Fe and V if these have been reduced by  $SO_2$  to  $Fe^{II}$  and  $V^{IV}$ . J. H. WATON

**3335. The analysis of industrial triphosphates. Determination of orthophosphate by paper chromatography in the presence of 32-labelled phosphorus.** P. Gauthier (*Bull. Soc. Chim. France*, 1955, [7-8], 981-983).—A solution of triphosphate (500 to 600 mg) containing orthophosphate,  $H_3^{32}PO_4$  ( $\approx 20 \mu C$ ) in 100 ml of water, is spotted quant. on to Whatman No. 30 paper and chromatographed, with dioxan (150 ml) - isopropanol (50 ml) -  $H_3BO_3$  (0.5 g) -  $H_2O$  (100 ml), adjusted to a pH of 7.2 to 7.3 with NaOH, as solvent. After being dried, the chromatogram is cut up in the region of the highest activity, and the orthophosphate is extracted and estimated colorimetrically with molybdate - hydrazine. The activity of the solution is compared with a standard to determine the recovery. The accuracy of the method and the difficulties are discussed. E. J. H. BIRCH

**3336. Phosphates in analytical chemistry. I. The qualitative properties of poly- and metaphosphates.** M. Shinagawa and M. Kobayashi (*J. Sci. Hiroshima Univ., A*, 1954, 18 [2], 237-244).—Results are tabulated of a qualitative investigation into the effects of the addition of phosphate (trimeta-, hexameta-, tri- or pyro-phosphate) on the ionic reaction in solution between a metal ion ( $Ag^+$ ,  $Pb^{2+}$ ,  $Hg^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Hg_2^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Sn^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ ,  $Al^{3+}$ ,  $Ba^{2+}$ ,  $Ca^{2+}$  or  $Mg^{2+}$ ) and any one of a no. of anions. Pentasodium triphosphate exerts a strong masking effect on certain reactions of each of the metal ions studied, and the hexameta-phosphate is effective in masking the reactions of the alkaline-earth metals. A. JOBLING

**3337. Use of rhodamine B in analytical chemistry. I. Determination of small quantities of antimony.** B. J. MacNulty and L. D. Woollard (*Anal. Chim. Acta*, 1955, 13 [1], 64-71).—Rhodamine B is used in a colorimetric method for the estimation of Sb. The Sb is first separated by co-pptn. with  $MnO_2$ , and is then oxidised to  $Sb^V$  with  $HClO_4$ . The complex is produced in the presence of HCl and  $M H_3PO_4$  by a 0.04 per cent. rhodamine-B soln. and is then extracted with benzene. The absorbancy of the benzene soln. is measured with a Spekker absorptiometer and yellow filters. The method gives a reproducibility with triplicate samples of  $\pm 10$  per cent. The only elements which interfere are Ti and large amounts of V. J. H. WATON

**3338. Spectrophotometric determination of bismuth with ethylenediaminetetra-acetic acid.** P. W. West and H. Coll (*Anal. Chem.*, 1955, 27 [8], 1221-1224).—From 2 to 25 p.p.m. of Bi can be determined quant. by measuring the u.v. absorption of the Bi complex with EDTA (disodium salt) (0.02 M) at 263.5  $m\mu$  in solutions adjusted to pH 0.8 to 1.2 with sodium acetate buffer. A blank is also run; the concn. of Bi is obtained from the calibration curve.  $Fe^{3+}$ ,  $Cu^{2+}$  and  $NO_3^-$  must be absent; an excess of  $Sb^{3+}$ ,  $Sn^{2+}$ ,  $Hg^{2+}$  or Pb interferes moderately in decreasing order; a pH of 1 (sulphate buffer) is preferred when these cations are present ( $PbSO_4$  is removed by centrifugation). If the concn. of Pb is  $> 50$  times that of Bi, perchlorate buffer should be used to avoid

adsorption of the bismuth complex by  $PbSO_4$ . The method is rapid and reliable. W. J. BAKER

**3339. Ultra-violet photometric titrations of bismuth and lead with ethylenediaminetetra-acetic acid.** R. N. Wilhite and A. L. Underwood (*Anal. Chem.*, 1955, 27 [8], 1334-1336).—The procedures described, which avoid serious interference from interactions of foreign cations with visual indicators, involve the u.v. photometric titration of perchlorate solutions of bismuth or lead ( $\approx 10^{-5}$  to  $10^{-6}$  M) with EDTA (0.01 or 0.001 M) at pH 2. The absorption max. are 240  $m\mu$  for the Pb complex and 265  $m\mu$  for the Bi complex. Bismuth and lead ( $\approx 0.5$  mg of each) can be determined simultaneously in one titration at 240  $m\mu$  because bismuth reacts first with the titrant. The specific effects of interfering ions in these u.v. photometric titrations are discussed. W. J. BAKER

**3340. Field determination of microgram amounts of niobium in rocks.** F. N. Ward and A. P. Marranzino (*Anal. Chem.*, 1955, 27 [8], 1325-1328).—From 50 to 2000 p.p.m. of niobium in rocks and soils can be determined rapidly in an aliquot ( $\approx 0.02$  to 0.04 g of sample) of the tartaric acid extract after decomposition of the rock with alkali bisulphate or pyrosulphate. To a 1- or 2-ml aliquot are added, with shaking, 5 or 5.6 ml of a soln. of tartaric acid (15 g) in 9 N HCl (100 ml), followed by 5 ml of aq.  $NH_4SCN$  (20 per cent.) and, within 5 min., 5 ml of ethyl ether. The yellow niobium thiocyanate complex in the ether extract is stabilised by addition of acetone (to make 10 ml of soln.) and the absorbance is measured photometrically at 385  $m\mu$ . The microgram content of Nb in the aliquot is read from a prepared calibration curve. Interference by  $> 1000 \mu g$  of Fe or Ti, or  $> 500 \mu g$  of V, is avoided by shaking the ether extract in succession with small amounts of  $SnCl_2$  in 2 N HCl before the final addition of acetone to the ether phase. More than  $\approx 200 \mu g$  of Mo or W, or both, cause high results, but neither U, Ta nor Bi interferes seriously. The error is within 5 per cent., and about 30 rocks can be analysed for niobium in one day. W. J. BAKER

**3341. Direct estimation of oxygen.** K. Drechkopf and B. Braukmann (*Brennstoffchem.*, 1955, 36 [13-14], 203-208).—A full description is given of an improved variation of the Unterzaucher method for the direct estimation of oxygen in solid and liquid compounds; the method is simpler, quicker, and gives the results automatically. The apparatus is described in detail. Instead of using a stream of N in a reverse direction during the introduction of the sample into the decomposition tube, the supply stream of N is divided, one part serving as gas for the decomposition and the other passing right through the apparatus (to prevent entry of air); this avoids errors and enables the apparatus to be left open for long periods. The quantity of C used for decomposing the reaction gases to CO is greatly reduced to avoid errors through side reactions, but a temp. of 1120°C is necessary. The O is not estimated by the iodimetric estimation of I released from  $I_2O_5$  by reaction with the gases, but by measuring the alteration in the electrical conductivity of NaOH soln., caused by the  $CO_2$  of the reaction gases (or the  $CO_2$  derived from their CO content). Tests of the method and apparatus with  $KHCO_3$  and with benzoic acid give accurate results. Substances containing S do not give satisfactory results. The possibility of obviating

this limit decomposition

3342. Improved Bradsh... 541).—The refinement of O in A of oxygen reagent +  $CO_2$  is p. NaOH so the alkali specially released extracted the use The rang p.p.m. c titrating  $Na_2S_2O_3$

3343. ions with Kém. F... tion is Erichro At the complex indicator soln. co to 5 ml) One dro  $NH_4$  sol by 6 to and 0-0 with K red with greenish EDTA. shaking quickly liquid change ppt. T the abs interfer phates

3344. dichrom (Paint A volu  $Na_2Cr_2$  chroma solution first to One dr the pin with E colourl confirm amount When is low. it can allowin particul solutio typicac observ great



this limitation by interposing heated Cu after the decomposition tube is being investigated.

H. L. WHITEHEAD

**3342. Determination of oxygen in certain gases. Improved Winkler method.** L. Silverman and W. Bradshaw (*Anal. Chim. Acta*, 1955, **12** [6], 526-541).—The Winkler method is adapted, by various refinements, to the determination of 1 to 150 p.p.m. of O in A, CO<sub>2</sub>, He, H and N. For the lower range of oxygen concn. the accuracy is 0.1 p.p.m. The reagent solutions are de-aerated by boiling while CO<sub>2</sub> is passed through them (He is used for the NaOH soln.). The reaction between the gas and the alkaline MnCl<sub>2</sub> is conducted *in vacuo* in a specially designed apparatus. The I that is released on acidifying the reaction product is extracted with *o*-xylene, and is determined with the use of the Beckman DU spectrophotometer. The range of the method can be extended to 2000 p.p.m. of O by taking smaller samples and by titrating the acidified reaction product with standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln.

W. C. JOHNSON

**3343. Rapid volumetric determination of sulphate ions with barium chloride.** E. Bakács (*Magyar Kém. Foly.*, 1955, **61** [2], 48-50).—The determination is carried out at pH 10. Indicators are Eriochrome black T and Mg<sup>++</sup> masked with EDTA. At the end-point, Ba<sup>++</sup> displace Mg<sup>++</sup> from the complex and the Mg<sup>++</sup> change the colour of the indicator from blue to wine-red. *Procedure*—A soln. containing 0.005 to 0.01 g of SO<sub>4</sub><sup>2-</sup> in H<sub>2</sub>O (3 to 5 ml) is diluted with 1.5 times its vol. of ethanol. One drop of methyl red soln. is added, then dil. aq. NH<sub>3</sub> soln. until the colour is pale yellow, followed by 6 to 8 drops of buffer (NH<sub>4</sub>Cl-aq. NH<sub>3</sub> soln.) and 0.015 to 0.020 g of Eriochrome black T mixed with KCl (1:100). The colour is changed to violet-red with 1 drop of 0.05 M MgCl<sub>2</sub> soln., then to greenish blue by the dropwise addition of 0.01 M EDTA. An equal vol. of CCl<sub>4</sub> is added and, while shaking, 0.01 M BaCl<sub>2</sub> is added dropwise, at first quickly, then slowly. Near the end-point the liquid is shaken after each drop. The colour change can be seen in the ring above the settled ppt. The determination can also be carried out in the absence of CCl<sub>4</sub>. The common cations do not interfere, neither do traces of Cl<sup>-</sup> or NO<sub>3</sub><sup>-</sup>. Phosphates can be determined in the same soln.

A. G. PETO

**3344. Estimation of sodium sulphate and sodium dichromate.** N. R. Kamath and N. F. Lewis (*Paintindia*, 1955, **5** [1] [Annual Number], 71-72).—A volumetric method of estimating Na<sub>2</sub>SO<sub>4</sub> in Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, based on titration of the neutralised chromate soln. with BaCl<sub>2</sub>, is described. An aq. solution of the sample is titrated with 0.1 N NaOH, first to bromophenol blue, then to phenolphthalein. One drop of 0.1 N acetic acid is added to discharge the pink colour, and the solution is then titrated with BaCl<sub>2</sub> solution until the supernatant liquid is colourless. The validity of the method has been confirmed by analysing mixtures containing known amounts of reagent-grade K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and K<sub>2</sub>SO<sub>4</sub>. When the total quantity of sulphate and chromate is low, the end-point is not sufficiently sharp, but it can be improved by warming the solution and allowing it to cool so that the finely dispersed particles cohere. Alternatively, a drop of the solution can be spotted on to filter-paper, when the typical yellow stain of chromate, if present, will be observed. Acidic starch paper may also be used for greater accuracy. The method is rapid and suitable

for routine estimation of sodium dichromate as a raw material for the manufacture of chrome-yellow and chrome-green pigments.

R. J. COLE

**3345. Vanadimetry. Estimation of thiosulphate.** H. Sanke Gowda, K. Bhaskara Rao and G. Gopala Rao (*Anal. Chim. Acta*, 1955, **12** [6], 504-514).—Thiosulphate can be oxidised quant. to tetrathionate by vanadate in the presence of H<sub>2</sub>SO<sub>4</sub>. The reaction is catalysed by Cu<sup>++</sup> but, with or without Cu<sup>++</sup>, the acid concn., time and temp. must be closely controlled. If acetic acid is substituted for H<sub>2</sub>SO<sub>4</sub>, much more latitude in conditions is permissible. *Procedure*—Add an aliquot of the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> soln. to an excess of 0.05 N NaVO<sub>3</sub> in 2 N to 8 N acetic acid containing 1 ml of 1 per cent. aq. Cu acetate, and set aside the soln. (now  $\approx$  50 ml) for 5 min.; add 5 ml of conc. H<sub>3</sub>PO<sub>4</sub>, increase the acetic acid concn., if necessary, to 5 N and titrate the excess of vanadate with standard Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, using diphenylbenzidine as indicator. Thiosulphate is also oxidised to tetrathionate by Fe<sup>+++</sup> in the presence of Cu<sup>++</sup>. The Fe<sup>++</sup> formed are then titrated with standard vanadate soln., diphenylbenzidine being used as indicator (*cf.* Lang and Kurtenacher, *Brit. Abstr. A*, 1942, 407). Vanadate oxidises S<sub>2</sub>O<sub>3</sub><sup>2-</sup> to SO<sub>4</sub><sup>2-</sup> if the reaction is carried out in 5 N HCl and in the presence of ICl. *Procedure*—Prepare the ICl soln. by dissolving 0.279 g of KI and 0.178 g of KIO<sub>3</sub> in 250 ml of water and diluting to 500 ml with conc. HCl (sp. gr. 1.18). Add 1 ml of this soln. to 20 ml of 0.25 N or 0.05 N NaVO<sub>3</sub>, then add the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> soln. and, with shaking, 30 ml of 10 N HCl during 1 min. Set aside for 10 min. and titrate the excess of vanadate with standard Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>, using diphenylbenzidine or N-phenylanthranilic acid as indicator.

W. C. JOHNSON

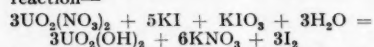
**3346. Determination of thiosulphate and sulphite in a galvanising bath containing copper cyanide.** G. Straub and S. A. Kiss (*Magyar Kém. Foly.*, 1955, **61** [2], 43-45).—To 10 to 15 ml of the soln. add 10 per cent. KCN soln. (5 ml). Heat at 110° to 120° C for 10 min. to convert the S<sub>2</sub>O<sub>3</sub><sup>2-</sup> into thiocyanate. To the cooled soln. add saturated aq. HgCl<sub>2</sub> soln. until it becomes opalescent (30 to 40 ml), then 2 ml in excess. Heat again at 110° to 120° C until the ppt. coalesces. Cool, filter, wash the ppt. with H<sub>2</sub>O (2 to 3 ml). Add 5 per cent. aq. FeCl<sub>3</sub>·6H<sub>2</sub>O soln. (20 ml) to the filtrate, dilute to 100 ml and, after 5 min., measure photometrically (S47 or S53 filter), comparing with a calibration curve. The error is  $\pm$  2 per cent., depending on the accuracy of the HgCl<sub>2</sub> addition. To determine SO<sub>3</sub><sup>2-</sup>, add 20 per cent. aq. BaCl<sub>2</sub> soln. (10 ml) to 5 ml of the soln. in a stoppered flask. After 15 min., filter the soln.; wash the ppt. with hot H<sub>2</sub>O (2  $\times$  10 ml). Return the ppt. and the filter to the flask, add 0.1 N iodine and 10 per cent. HCl (20 ml). Stopper the flask, shake for 10 min. and back-titrate with 0.1 N S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, using starch. To obtain the true value for SO<sub>3</sub><sup>2-</sup>, add 5.5 per cent. to the value found. The error is  $<$  -1 per cent. Anions other than S<sub>2</sub>O<sub>3</sub><sup>2-</sup> do not interfere but, if it is present, SO<sub>3</sub><sup>2-</sup> is obtained by difference.

A. G. PETO

**3347. Conditions for the formation of blue molybdosilicic heteropolyacid.** M. L. Tsap (*Zavod. Lab.*, 1955, **21** [3], 281-285).—The effect of pH on the formation of molybdenum blue was studied by mixing 3 to 3.5 ml of citrate buffer with 0.5 ml of 0.006 M ammonium molybdate and 0.5 to 1.0  $\mu$ g of Si as sodium silicate, then adding 0.5 ml of 0.001 M 1-amino-2-naphthol-4-sulphonic acid. The soln.

was diluted to 5 ml with water, and examined photometrically at 825 to 837  $m\mu$ . The optimum absorption occurs at pH 1.9 to 3.0. Phosphate and arsenate in amounts up to 100 times that of silicate do not interfere. Metol can be used nearly as satisfactorily as reducing agent. The molar absorption coeff. is  $1.1 \times 10^4$ . G. S. SMITH

**3348. Iodimetric determination of uranium.** G. S. Deshmukh and M. K. Joshi (*Chem. Ber.*, 1954, **87** [10], 1446-1448).—The hydrolysis of uranyl salts by KI-KIO<sub>3</sub> solutions is demonstrated. The reaction—



is quant. completed at pH 4.2 to 4.3 in the presence of an excess of KI-KIO<sub>3</sub> and carbon tetrachloride at 60° to 70° C under reflux on a water bath for 15 min. Titration of the free I with  $\text{N Na}_2\text{S}_2\text{O}_3$  or  $\text{N As}_2\text{O}_3$  affords a quant. determination of U.

D. R. GLASSON

**3349. Uranyl-alizarin red S complex. A spectrophotometric study.** K. S. Venkateswarlu and B. S. V. Raghava Rao (*Anal. Chim. Acta*, 1955, **13** [1], 79-82).—The violet complex given by uranyl salts and alizarin red S in neutral or weakly alkaline soln. gives an absorption max. at 570  $m\mu$ , whilst the reagent itself has a max. at 520  $m\mu$ . The complex is shown to be a stoichiometric compound of  $\text{UO}_2^{2+}$  and alizarin red S in the ratio 1:1, having its max. stability at  $\approx$  pH 8.1. On applying Kuhn's equation to the structure of the reagent and the complex, absorption peaks are calculated to occur at 527 and 585  $m\mu$ , respectively.

J. H. WATON

**3350. Determination of microgram quantities of fluoride by measurement of current from spontaneous electrolysis.** B. B. Baker and J. D. Morrison (*Anal. Chem.*, 1955, **27** [8], 1306-1307).—Instantaneous current readings in spontaneous (internal) electrolysis can be used to calculate the concn. of one of the reactants in the cell. The procedure is accurate only for  $\mu\text{g}$  amounts, and good results can be obtained for  $\text{CN}'$  in the cell  $\text{Ag} | 0.1 \text{ M NaOH} | \text{Pt}$  and for  $\text{F}'$  in the cell  $\text{Al} | 0.2 \text{ M acetic acid} | \text{Pt}$ . In the former cell, when the electrodes are lowered the momentary blank current becomes zero within  $\approx 1$  min., but addition of  $\text{CN}'$  yields an approx. exponential current-time curve; the current is read after 1 min. This cell can be used to detect and determine HCN in air since the NaOH soln. serves as absorbent and can then be transferred directly to the cell. The concn. of  $\text{CN}'$  should not exceed  $2 \times 10^{-3} \text{ M}$ ; interference is caused by  $\text{OCl}'$  and  $\text{S}''$ . In the second cell, the blank current is usually from 5 to 10  $\mu\text{A}$ , but addition of  $\text{F}'$  causes a rapid increase followed by a uniform decrease; the current is read after 2 min. For amounts of  $\text{F}' < 5 \mu\text{g}$ , 0.017 M benzoic acid is the preferred electrolyte;  $> 1000 \mu\text{g}$  of  $\text{Cl}'$  interfere seriously, whilst  $\text{PO}_4'''$  and  $\text{H}_2\text{S}$  cause some variation. The sensitivity is 1 p.p.m. of fluorine, so the cell can be used for samples of fluorinated water, provided that large amounts of  $\text{Cl}'$  are absent. Since the current depends on rate of stirring, cell size and history, each of the cells must be calibrated against standard solutions of cyanide and fluoride. The construction, operation and calibration of the cells are described.

W. J. BAKER

**3351. Leaded-glass test for fluoride.** A. Viswanathan and S. Azmatullah (*Chemist Analyst*, 1955, **44** [1], 28).—One end of a soda-glass rod is coated

with a thin paste of lead oxide and water and heated in an oxidising flame until the coating becomes transparent. The rod is then re-heated in a reducing flame until an area of metallic lead appears on the surface. If the rod is held in the vapour evolved from a sample acidified with  $\text{H}_2\text{SO}_4$  and warmed, the disappearance of the black colour indicates the presence of a fluoride. This is best observed by washing the rod with water. One rod may be used repeatedly, as the metallised surface is restored by re-heating in a reducing flame.

D. LIFF

**3352. Colorimetric determination of the perchlorate ion.** W. Bodenheimer and H. Weiler (*Anal. Chem.*, 1955, **27** [8], 1293-1295).—The slight solubility of cupric tetrapyrindine perchlorate in  $\text{H}_2\text{O}$  excludes a gravimetric determination of  $\text{ClO}_4'$  by this means, but solutions of cupric tetrapyrindine salts in aq. pyridine show a deep-blue colour, the intensity of which decreases as part of the complex is pptd. as perchlorate. For the procedures described, solution A is prepared by dissolving  $\approx 25 \text{ g}$  of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in water, adding 450 ml of pyridine and making up to 1 litre with water. Stored in a brown bottle this soln. is stable for 2 years. Solution B is aq. NaCl (20 per cent.). Procedure—For inorg. perchlorates, a weighed amount of sample is added to 2 ml of soln. A, followed by 20 ml of soln. B, and water to make 25 ml. After 48 hr. the absorbance of the supernatant soln. is measured in a Beckman DU spectrophotometer at 635  $m\mu$ , the concn. of  $\text{ClO}_4'$  being obtained from a calibration curve. For org. perchlorates, the sample is dissolved in  $\text{H}_2\text{O}$  to a concn. of 50 to 600  $\mu\text{g}$  of  $\text{ClO}_4'$  per ml, 2 ml of soln. A are added and the soln. is made up to 25 ml (or a lesser vol. if suitable). This soln. is shaken with an excess of dry NaCl, kept for 24 hr. and filtered. The absorbance of the filtrate is measured in a colorimeter with filter 66 (transmission range from 640 to 700  $m\mu$ ). At concn. of 0.5 to 1.2 mg of inorg. perchlorate per ml, the error is from 1 to 2 per cent., whilst  $< 100 \mu\text{g}$  of org. perchlorate per ml can be determined to within 5  $\mu\text{g}$ . Other ions do not interfere unless in concn.  $> 10 \text{ mg}$  per ml.

W. J. BAKER

**3353. Thioacetamide in the separation and compleximetric determination of manganese.** H. Flaschka and H. Abdine (*Chemist Analyst*, 1955, **44** [1], 8-9).—An excess of aq. thioacetamide solution is added to a neutral or slightly acidic solution of manganese, followed by  $\text{NH}_4\text{Cl}$  and sufficient concn. aq.  $\text{NH}_3$  to make the solution distinctly alkaline. After boiling for  $\approx 3$  min. the solution is filtered through a porous porcelain crucible. The ppt. is washed with water, dissolved in dil. HCl, and the solution is diluted to  $\approx 50 \text{ ml}$ . Hydrogen sulphide is boiled off, and when the soln. is cool  $\approx 3 \text{ mg}$  of ascorbic acid and one drop of methyl red are added. Sufficient aq.  $\text{NH}_3$  is added to give a distinct yellow colour. Buffer solution is added and enough Eriochrome black T indicator powder to give a clearly visible red colour. Finally the solution is titrated with standard EDTA (disodium salt) until the indicator changes to a pure blue-green.

D. LIFF

**3354. Rapid determination of manganese in metal alloys. I. Volumetric-potentiometric perchloric acid-orthophosphoric acid method.** H. Schröder (*Metall.*, 1954, **8** [13-14], 542-543).—The  $\text{Mn}^{II}$  is oxidised in the presence of  $\text{H}_2\text{PO}_4$  to  $\text{Mn}^{III}$  by means of  $\text{HClO}_4$ . The  $\text{Mn}^{III}$  is then quant. reduced

with  $\text{Fe}^{II}$  metrically, does and for Mn has applicable brass, aluminium, 20 min.

**3355. Vanadate and oxalic acid.** (*Anal. Chem.*, 1955, **27** [8], 1293-1295).—The slight solubility of cupric tetrapyrindine perchlorate in  $\text{H}_2\text{O}$  excludes a gravimetric determination of  $\text{ClO}_4'$  by this means, but solutions of cupric tetrapyrindine salts in aq. pyridine show a deep-blue colour, the intensity of which decreases as part of the complex is pptd. as perchlorate. For the procedures described, solution A is prepared by dissolving  $\approx 25 \text{ g}$  of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in water, adding 450 ml of pyridine and making up to 1 litre with water. Stored in a brown bottle this soln. is stable for 2 years. Solution B is aq. NaCl (20 per cent.). Procedure—For inorg. perchlorates, a weighed amount of sample is added to 2 ml of soln. A, followed by 20 ml of soln. B, and water to make 25 ml. After 48 hr. the absorbance of the supernatant soln. is measured in a Beckman DU spectrophotometer at 635  $m\mu$ , the concn. of  $\text{ClO}_4'$  being obtained from a calibration curve. For org. perchlorates, the sample is dissolved in  $\text{H}_2\text{O}$  to a concn. of 50 to 600  $\mu\text{g}$  of  $\text{ClO}_4'$  per ml, 2 ml of soln. A are added and the soln. is made up to 25 ml (or a lesser vol. if suitable). This soln. is shaken with an excess of dry NaCl, kept for 24 hr. and filtered. The absorbance of the filtrate is measured in a colorimeter with filter 66 (transmission range from 640 to 700  $m\mu$ ). At concn. of 0.5 to 1.2 mg of inorg. perchlorate per ml, the error is from 1 to 2 per cent., whilst  $< 100 \mu\text{g}$  of org. perchlorate per ml can be determined to within 5  $\mu\text{g}$ . Other ions do not interfere unless in concn.  $> 10 \text{ mg}$  per ml.

**3356. Estimation of Taimni** 1955, **12** as  $\text{Re}_2\text{O}_7$ , perhenate alkali sub of  $\text{HClO}_4$  amount of the ppt. collected, washed and dried, heated to precipitate sodium of a low temp. soln. of ppt. red and the determine mine  $\text{Hg}$  to produce or ammo ( $< 5^\circ \text{C}$ ) and allowed successive dried at

**3357. 4-amino** F. Szab 131-142 available oxidised violet m ditions 1 are inv contain 1 ml of to  $\approx$  p is alrea for 5 m 570  $m\mu$



with  $\text{Fe}^{II}$  (as  $\text{FeSO}_4$ ) visually or, better, potentiometrically. Chromium does not interfere but V does and must be determined after the titration for Mn has been carried out. The procedure is applicable to the determination of Mn in cast iron, brass, aluminium alloys and ferromanganese (76 per cent. of Mn); a single determination takes 15 to 20 min.

METALL. ABSTR.

**3355. Volumetric estimation of potassium permanganate and potassium dichromate in mixtures with oxalic acid.** G. Gopala Rao and U. Muralikrishna (*Anal. Chim. Acta*, 1955, **13** [1], 8-11).—Potassium permanganate can be estimated in the presence of  $\text{K}_2\text{Cr}_2\text{O}_7$  by titrating with a standard soln. of sodium oxalate or oxalic acid. The titration is carried out at room temp. in the presence of  $\text{H}_2\text{SO}_4$  and  $\text{MnSO}_4$ . The  $[\text{H}^+]$  should be  $\approx 2\text{N}$ , and the  $\text{MnSO}_4 \approx 5 \times 10^{-5}\text{M}$ . The colour change at the end-point from orange-red to yellow is quite sharp. The reverse titration with the oxalate in the flask gives inaccurate results, since a reaction between oxalic acid and  $\text{K}_2\text{Cr}_2\text{O}_7$  is induced by the reaction between oxalic acid and  $\text{KMnO}_4$ . When the  $\text{KMnO}_4$  has been estimated,  $\text{H}_3\text{PO}_4$  and diphenylbenzidine indicator are added, and the  $\text{K}_2\text{Cr}_2\text{O}_7$  is determined with standard  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ .

J. H. WATON

**3356. Estimation of metals as sulphides. III. Estimation of rhenium, silver and mercury.** I. K. Taimni and G. B. S. Salaria (*Anal. Chim. Acta*, 1955, **12** [6], 519-525).—Rhenium is precipitated as  $\text{Re}_2\text{S}_7$  when conc. HCl is added to a soln. of perrhenate previously treated with an excess of alkali sulphide to form a thio salt. The final concn. of HCl should be  $\approx 6\text{N}$ . By adding a large amount of  $(\text{NH}_4)_2\text{SO}_4$  and heating to boiling point, the ppt. is obtained in a filterable form. It is collected in a sintered-glass crucible (porosity 4), washed successively with water, alcohol and ether, and dried in a vacuum-desiccator. It can be heated to  $160^\circ\text{C}$  without loss in wt. Silver is precipitated as  $\text{Ag}_2\text{S}$ , free from sulphur, if the sodium or ammonium sulphide soln. is prepared at a low temp. (cf. *Anal. Abstr.*, 1954, **1**, 2391). A soln. of  $\text{AgNO}_3$  is treated with aq.  $\text{NH}_3$  until the ppt. redissolves, an excess of sulphide soln. is added and the ppt. is coagulated by shaking. The determination is completed as for Re. To determine Hg, a soln. of  $\text{HgCl}_2$  is treated with aq.  $\text{NH}_3$  to produce a slight turbidity, an excess of sodium or ammonium sulphide soln. (prepared at a temp.  $< 5^\circ\text{C}$ ) is added, the soln. is acidified with aq. HCl and heated to boiling point; the pptd.  $\text{HgS}$  is allowed to settle, it is then filtered off, washed successively with water, alcohol and ether, and dried at  $105^\circ\text{C}$ .

W. C. JOHNSON

**3357. Colorimetric determination of iron using 4-amino-4'-methoxydiphenylamine.** L. Erdey and F. Szabadváry (*Acta Chim. Hung.*, 1955, **6** [1-2], 131-142).—4-Amino-4'-methoxydiphenylamine (I), available commercially as Variamine blue base, is oxidised by  $\text{Fe}^{+++}$  and certain other ions to a blue-violet merquinoid compound. The optimum conditions for the determination of  $\text{Fe}^{+++}$  by this means are investigated. A feebly acid solution, 25 ml, containing 50 to 300  $\mu\text{g}$  of  $\text{Fe}^{+++}$ , is treated with 1 ml of a filtered 1 per cent. solution of I, adjusted to  $\approx \text{pH } 3$  with an acetate buffer (unless the pH is already between 1 and 4), shaken and set aside for 5 min. before measuring the extinction at 570  $\mu\text{m}$ . The extinction increases linearly with

concn. over the range 0.2 to 12.0  $\mu\text{g}$  per ml. The optical density is 0.11 for 1  $\mu\text{g}$  per ml. Determinations can be made in the presence of comparable amounts of  $\text{V}^{+}$ ,  $\text{CrO}_4^{--}$ ,  $\text{VO}_3^{--}$ ,  $\text{MnO}_4^-$  and  $\text{NO}_3^-$  by measuring the extinction before and after addition of citrate. Disturbing effects are produced by  $\text{Fe}^{++}$ , Bi and Sn $^{++}$ , and by very large amounts of Zn, Cd or Pb; Na, K, Mg,  $\text{NH}_4^+$ , Ca, Ba, Mn $^{++}$ , Ni, Co, Al, Cu, As and Sb do not interfere. Anions that form complexes with  $\text{Fe}^{+++}$  must be absent. The method can be applied to the analysis of a Pb-Sb alloy containing Zn and Ni. A 5-g sample is dissolved in 50 ml of hot conc. HCl, evaporated to dryness with 2 g of KCl, dissolved in 50 ml of hot HCl (1 + 1), cooled, and filtered. The filtrate is treated hot with  $\text{H}_2\text{S}$ , and the resulting ppt. is filtered off. An aliquot portion of the filtrate is oxidised with  $\text{H}_2\text{O}_2$ , evaporated down and treated with I as above.

A. B. DENSHAM

**3358. Amperometric titration of iron with 1-nitroso-2-naphthol.** R. F. Wilson and H. G. Lovelady (*Anal. Chem.*, 1955, **27** [8], 1231-1233).—Amperometric titrations of  $\text{Fe}^{+++}$  (0.002 to 0.05 millimoles) can be made directly with 1-nitroso-2-naphthol in 2 M acetic acid-acetate buffer at  $-0.5\text{V}$  against the S.C.E. at  $25^\circ\text{C}$ . The precision (on duplicates) is  $\pm 0.1$  per cent. and the error is within 0.3 per cent. The method is applicable to ores (10 to 30 per cent. of Fe); if Pb is present in the acid soln. obtained after decomposition of the ore, iron must be separated therefrom by ether extraction. *Procedure*—To an aliquot of the iron soln. in a 100-ml flask, add 0.2 per cent. aq. gelatin (5 ml), buffer soln. (20 ml) and 95 per cent. ethanol (20 ml) and make up to vol. with water. Transfer 20 ml from the flask to an H-type cell and pass pure nitrogen through for 15 min. (The nitrogen should be conditioned by passage through a soln. containing all the reagents except iron and the titrant.) Then wait until the current is const. before adding a few drops of 1-nitroso-2-naphthol soln. ( $\approx 0.09\text{M}$ ), stir with nitrogen for 1 min. and take the current reading 3 min. later. Repeat with successive additions of titrant, waiting 2 min. before taking each reading. Duplicate titrations should be done on each soln. The procedure can be applied to certain steels.

W. J. BAKER

**3359. Determination of iron with mercurous nitrate in the presence of chlorides.** V. M. Tarayan and M. G. Ekimyan (*Zavod. Lab.*, 1955, **21** [3], 304-305).—High results obtained in the mercurous nitrate titration of Fe in the presence of Cl $^-$  are due to the formation of difficultly soluble  $\text{Hg}_2\text{Cl}_2$ . Addition of a suitable amount of  $\text{NH}_4\text{SCN}$  decomposes the  $\text{Hg}_2\text{Cl}_2$  and enables correct results to be obtained. To determine Fe in silicates, 0.5-g of sample is fused with 1 g of  $\text{Na}_2\text{CO}_3$ , the melt is dissolved in 0.4 N  $\text{H}_2\text{SO}_4$ , 0.3 N  $\text{HNO}_3$  or 2 N HCl. The solution is diluted with water to a vol. of 100 to 150 ml, 15 to 20 ml of 40 per cent.  $\text{NH}_4\text{SCN}$  solution are added, and the Fe is titrated with 0.1 N  $\text{Hg}_2(\text{NO}_3)_2$ . Results are independent of the nature of the acid used.

G. S. SMITH

**3360. Separate determination of metallic iron, ferrous oxide and ferric oxide when present together.** N. I. Stognil and A. G. Kirilenko (*Zavod. Lab.*, 1955, **21** [3], 294-298).—The method with  $\text{CuSO}_4$  [dissolution of metallic Fe in  $\text{CuSO}_4$  soln. neutralised by the addition of  $\text{Cu}(\text{OH})_2$  suspension] gives high results for the metallic iron content in a mixture of Fe, FeO and  $\text{Fe}_2\text{O}_3$ , because of the hydrolysis of

$\text{CuSO}_4$ , and the consequent dissolution of part of the oxides. Addition of  $\text{K}_2\text{SO}_4$  suppresses the hydrolysis and enables accurate results to be obtained. To determine Fe in admixture with its oxides, 0.5 g is dissolved, in an atmosphere of  $\text{CO}_2$ , in 40 ml of 15 to 16 per cent.  $\text{CuSO}_4$  soln. containing 6 g of  $\text{K}_2\text{SO}_4$ . After being boiled for 15 min., the solution is filtered from the oxides and the pptd. Cu, and the filtrate, together with water washings, is freed from Cu by boiling it with 15 ml of conc.  $\text{H}_2\text{SO}_4$  in the presence of two spirals of aluminium wire (10 mm in diameter, 30 to 35 mm in length). The solution is again filtered, 15 ml of a soln. containing 150 ml of conc.  $\text{H}_2\text{SO}_4$  and 130 ml of  $\text{H}_3\text{PO}_4$  (sp. gr. 1.70) in 1 litre of water are added, and the Fe is titrated with 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  in the presence of 2 ml of Na diphenylaminesulphonate indicator. To determine the oxides, 0.25 g of the material is dissolved as described above, and the Cu, pptd. with the oxides, is collected on asbestos in a Gooch crucible. The ppt., together with the asbestos, is transferred to a tube with a conical bottom and is treated with 15 to 20 ml of a soln. of 360 g of  $(\text{NH}_4)_2\text{CO}_3$  in 1 litre of aq.  $\text{NH}_3$  (1 + 4). Air is passed for 20 min. through a capillary tube reaching to the bottom of the tube and the soln. is then filtered by suction through a glass filter immersed in the soln. The oxides, after being washed with ammoniacal ammonium carbonate soln. and then with water, are dissolved in the same vessel in 15 ml of dil.  $\text{H}_2\text{SO}_4$  (1 + 3) and 1 ml of conc. HCl at  $100^\circ\text{C}$ , with a current of  $\text{CO}_2$  passing through the capillary for 20 min. The filtering tube is removed and washed, the soln. is filtered, mixed with 15 ml of a soln. containing 65 g of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 135 ml of  $\text{H}_3\text{PO}_4$  (sp. gr. 1.70) and 130 ml of conc.  $\text{H}_2\text{SO}_4$  in 1 litre of water, and titrated with 0.1 N  $\text{KMnO}_4$  for  $\text{Fe}^{++}$ . The total Fe in the solution is then determined in the titrated solution after reduction, and the  $\text{Fe}^{+++}$  originally present are found by difference.

G. S. SMITH

**3361. The photometric determination of iron in aluminium alloys.** H. Jackson, R. E. Bailey and L. H. Williams (*Metalurgia*, 1955, **51**, 309-311).—A photometric method is described for the determination of Fe in pure aluminium, all types of aluminium alloys, and hardeners, using a mixed reagent (1:1:3) of a 1 per cent. soln. of hydroxylamine, a 0.15 per cent. soln. of o-phenanthroline monohydrate, and acetate buffer. This reagent is stable and the method is free from interference from normal alloying elements. The accuracy of the method is satisfactory. *Procedure*—Millings (0.1 g) are treated with 10 ml of NaOH soln. (20 per cent.). When the attack is complete the soln. is washed down and boiled gently for 2 to 3 min. For high-silicon alloys (> 4 per cent.) a heating period of 20 min. or more is required before boiling to oxidise the Si. After a further washing down, the soln. is diluted to approx. 25 ml, 15 ml of HCl are added, and the soln. is mixed and boiled gently for 10 min. It is then cooled, filtered through a Whatman No. 4 filter-paper into a 200-ml calibrated flask, diluted to volume, and mixed well. A 25-ml aliquot is then transferred by pipette into a 100-ml calibrated flask, to which 25 ml of the mixed reagent are added. The soln. is then diluted to 100 ml and mixed well. The extinction is measured on a Spekker absorptiometer, a mercury lamp and Ilford 603 and Chance ON 13 (or ON 20) filters with 4-cm cells being used. A blank determination is carried out on the reagents and the same aliquot is used as for the sample. The Spekker

absorptiometer is calibrated by passing aliquots, by pipette (up to 15 ml), of a standard soln. of Fe (1 ml = 0.01 mg of Fe) into a series of 100-ml calibrated flasks. After diluting, adding 25 ml of mixed reagent, and diluting to volume, extinctions are measured. A plot of extinctions against the nominal iron contents is linear.

G. C. JONES

**3362. Methods for the analysis of iron and steel.** XXXIII. Iron in ores, slags and refractories. British Standards Institution (B.S. 1121: Part 33: 1955, 10 pp.).—*Volumetric method*—The dried sample (0.50 g) is dissolved in HCl, and the soln. is fumed with  $\text{H}_2\text{SO}_4$ . After oxidation with 0.05 per cent.  $\text{KMnO}_4$  soln., the Fe is reduced with  $\text{H}_2\text{S}$ , the generator being fitted with a trap to prevent iron salt from entering the soln. The soln. is filtered and the excess of  $\text{H}_2\text{S}$  is boiled off, then  $\text{H}_3\text{PO}_4$  and barium diphenylamine indicator are added and the Fe is titrated with 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. A blank should be performed. Replicate determinations on samples containing  $\approx 50$  per cent. of Fe should not differ by > 0.25 per cent. The method is modified for material with smaller percentages of Fe. The sample is treated with HCl and HF, and any residue is ignited and fused with  $\text{KHSO}_4$ . The filtrate, after leaching out the melt, is added to the main bulk. The method is then as described above, except that 0.02 N  $\text{K}_2\text{Cr}_2\text{O}_7$  soln. and pre-oxidised sodium diphenylaminesulphonate are used in the titration. A reproducibility of  $\pm 0.02$  per cent. of Fe may be expected on material containing 0.05 to 2.0 per cent. of Fe for a 2-g sample, and  $\pm 0.05$  per cent. of Fe on material containing 2.0 to 5.0 per cent. for a 1 per cent. sample. *Absorptiometric method*—The sample (0.5 g) is dissolved as outlined in the modified volumetric procedure. The filtrate is made up to 250 ml, and 20-ml aliquots are used (40 ml if the sample contains 0.2 per cent. of Fe). Two ml of a 20 per cent. citric acid soln., 1 ml of a 10 per cent. thioglycolic acid soln. and 6 ml of 50 per cent. aq.  $\text{NH}_3$  soln. are added and the soln. is made up to 50 ml. The light absorption is measured in 2- or 4-cm cells in a Hilger photo-electric absorptiometer, employing the mercury-vapour lamp and Ilford 605 and Calorex H.503 filters. Replicate determinations should not differ by >  $\pm 0.01$  per cent. for < 0.2 per cent. of total Fe, nor by >  $\pm 0.02$  per cent. for > 0.2 per cent. of total Fe.

J. H. WATON

**3363. Quantitative spectrographic analysis of fireclay for ferric oxide, titanium dioxide, magnesium oxide and calcium oxide in solutions.** Yu. A. Sherstkov (*Zavod. Lab.*, 1955, **21** [3], 320-324).—An improved sparking device (fulgurator) is described. The lower electrode is a specially shaped carbon rod projecting above the surface of the solution. Light is carried up to the end through a central channel. Spectra taken at 15-sec. intervals over a period of 165 sec. show that with this electrode the relative intensity of the lines Ca 3968 Å and Co 3894 Å remains nearly constant, whilst those with the normal electrode without capillary show fairly considerable variations. Excitation is by a Ralskil spark. Results obtained for the  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , MgO and CaO contents of samples of fireclay are given.

G. S. SMITH

**3364. Method of selecting samples for the determination of ferrous and ferric oxides in solidified slag.** M. Ya. Medzhibozhskii (*Zavod. Lab.*, 1955, **21** [3], 289-294).—In taking a sample of slag from a basic open-hearth furnace much of the ferrous

oxide is composed from that massive slag to that of the door, from not less than

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3367. I the deter W. F. S Chem., eliminati during t

oxide is oxidised by the air to ferric oxide; the composition of the solidified slag therefore differs from that of the liquid slag in the bath. To minimise oxidation, the sample should be poured into a massive sampler with a horizontal channel similar to that of the viscometer used for testing the slag, and the slag should be taken through the middle door, from the middle layer of slag, and at a distance not less than 1 metre from the charging door.

G. S. SMITH

**3365. Coulometric determination of ferrocyanide with electrolytically generated ceric ion.** R. V. Dilts and N. H. Furman (*Anal. Chem.*, 1955, **27** [8], 1275-1277).—By adopting the sensitive amperometric end-point procedure (*Brit. Abstr. C*, 1951, 431), coulometric titrations of 0.5 to 30 mg of  $K_4Fe(CN)_6$  with electrolytically generated  $Ce^{IV}$  can be made with an error of  $\pm 0.4$  per cent. The full procedure described is based on the Furman-Evans method (*Brit. Abstr. A*, 1929, 669). As the chemical reaction near the equivalence point is slow, it is necessary to generate in small increments in this region and to wait 5 to 10 min. for equilibrium to become established. The pre-set potential across the indicator electrodes is 1.210 V; the const. current can vary from 25  $\mu A$  to 25 mA according to the concn. of  $K_4Fe(CN)_6$ . The samples should preferably be weighed aliquots of 0.01 N  $K_4Fe(CN)_6$  because solutions more dil. than 0.001 N are unstable.

W. J. BAKER

**3366. The photometric determination of cobalt by extraction with 2-nitroso-1-naphthol.** A. Claassen and A. Daamen (*Anal. Chim. Acta*, 1955, **12** [6], 547-553).—The method of Baron (*Anal. Abstr.*, 1954, **1**, 489) is modified for the analysis of ferrous and non-ferrous alloys. *Procedure*—To a soln. of the sample, containing  $\pm 0.2$  mg of Co, in dil. acid, add sufficient aq. Na citrate (40 per cent. w/v) to keep ter- and quadri-valent metals in soln., dilute to between 50 and 75 ml and adjust to pH 3 to 4 by adding 2 N HCl or 2 N NaOH. Add 10 ml of aq.  $H_2O_2$  (3 per cent.) and, after a short interval, 2 ml of a 1.0 per cent. acetic acid soln. of 2-nitroso-1-naphthol, which has been previously shaken with 1 g of activated charcoal and filtered. Set aside for  $< 30$  min. and then shake the soln. vigorously for 1 min. with 25 ml of  $CHCl_3$ ; separate, and repeat the extraction twice with 10-ml quantities of  $CHCl_3$ . Dilute the combined extracts with  $CHCl_3$  to 50 ml and shake this soln. with 20 ml of 2 N HCl for 1 min.; separate, and shake the chloroform layer with 2 N NaOH for 1 min. Repeat the extraction with 2 N NaOH. Filter the chloroform soln. through cotton wool and determine the optical density at 530  $m\mu$ . Determine, and apply, the correction for a blank, and prepare a calibration curve with known quantities of Co. Metals of the Pt group, Pd and Au must be absent; Fe and Sn must be oxidised to  $Fe^{III}$  and  $Sn^{IV}$ , respectively, in the original soln.; Cu in excess of 25 mg must be removed (electrolytically); ammonium salts in excess of 1 g cause low results; when  $> 100$  mg of Ni are present the pH of the soln., after adding the reagent, should be between 3.0 and 3.8, and a further 2 ml of reagent soln. is added for every 250 mg of Ni.

W. C. JOHNSON

**3367. Nature and elimination of interferences in the determination of cobalt with nitroso-R salt.** W. F. Shipmen, S. C. Foti and W. Simon (*Anal. Chem.*, 1955, **27** [8], 1240-1245).—Procedures for eliminating the interference of certain elements during the electrophotometric determination of

cobalt with nitroso-R salt (**I**) in solutions buffered to pH 5.5 with acetic acid-acetate buffer have been studied, and a simple rapid method of determination without interferences has been devised for general use. The following ions, when present variously in amounts from 40 to 2400  $\mu g$ , interfere seriously by forming complexes with **I**:  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ce^{IV}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$ ,  $Sn^{2+}$ ,  $VO^{2+}$  and  $Cu^{2+}$ , as well as  $Cr^{VI}$ . Correct absorbances (with a 525- $m\mu$  filter) are obtained if the sample solutions are previously brominated and treated with 33 per cent. aq. KF (to complex the interfering ion) before the addition of **I**.

W. J. BAKER

**3368. Quantitative determination of cobalt with the rotating mercury electrode.** P. S. Tutundžić and D. Stojković (*Anal. Chim. Acta*, 1955, **12** [6], 580-585).—A rotating mercury electrode previously described (*Brit. Abstr. A*, 1932, 243) is modified so that the electrode and the electrolyte container rotate as one unit. Electrolysis times are thus shortened. Only 16 to 25 g of mercury are required, and 27 to 216 mg of Co can be deposited in 40 to 75 min. from 10 to 15 ml of  $CoSO_4$  soln. containing 0.05 to 0.2 ml of conc.  $H_2SO_4$ , a current of 2 amp. being used. The error, calculated on the average of six determinations, varies from  $-0.12$  to  $-0.29$  per cent.

W. C. JOHNSON

**3369. Rapid determination of cobalt in alloy steels by the tetraphenylarsonium method.** L. P. Pepkowitz and J. L. Marley (*Anal. Chem.*, 1955, **27** [8], 1330-1331).—By slightly modifying the procedure used by Potratz *et al.* (*Brit. Abstr. C*, 1952, 197) for the spectrophotometric determination at 620  $m\mu$  of Co as tetraphenylarsonium cobaltothiocyanate in  $CHCl_3$  soln., the method can be extended to 18:8 stainless steels, Inconels, Ni, Cr, and boron carbide. The accuracy is  $\pm 0.001$  per cent. *Procedure*—Evaporate to dryness an aliquot (50 to 150  $\mu g$  of Co) of the soln. obtained from the acid dissolution of the steel (0.5 to 1 g), dissolve the cool residue in a few drops of conc. HCl and again evaporate to dryness. Dissolve the residue in a min. vol. of HCl (1 + 1), add  $\approx 15$  ml of  $H_2O$  and nearly neutralise the soln. with aq.  $NH_3$  (1 + 1). Then add successively, with stirring, 3 to 4 drops of aq.  $K_2S_2O_8$  (10 per cent.), 10 ml of aq.  $NH_4SCN$  (50 per cent.) and solid  $NH_4F$  (1.5 g) to complex interfering elements (Fe, Cu, Mo, V) and to form the cobaltothiocyanate complex. Transfer the soln. to a separating funnel, add 15 drops of 0.05 M tetraphenylarsonium chloride soln. (**I**) and extract the coloured complex with  $CHCl_3$  (19 ml), making three extractions and adding a further 10 drops of **I**. Measure the absorbance of the filtered  $CHCl_3$  layers (made up to 25 ml), correct this value for the reagent blank, and read the concn. of Co from the calibration curve.

W. J. BAKER

**3370. Determination of nickel. Development of a method applicable to all classes of steel.** Methods of Analysis Committee, B.I.S.R.A. (*J. Iron St. Inst.*, 1955, **180** [3], 262-269).—Investigations of methods for the determination of Ni in steel, with special reference to interference by Cu and Co, have resulted in the formulation of two methods. If  $> 0.15$  g of Cu + Co is present in the sample taken (containing  $> 0.04$  g of Ni) the sample is dissolved in HCl and oxidised with  $HNO_3$ ; the Ni is pptd. with dimethylglyoxime from ammoniacal citrate soln. The filtered complex is dissolved in  $HNO_3$  and evaporated to fuming with  $H_2SO_4$ ; the residue is dissolved in water, citric acid is added, then excess

of aq.  $\text{NH}_3$ . The Ni is determined by a cyanargentimetric titration after adding KI soln. The reproducibility is  $\pm 0.02$  per cent. at 3 per cent. of Ni,  $\pm 0.10$  per cent. at 15 per cent. of Ni, and  $\pm 0.30$  per cent. at 70 per cent. of Ni. For high-cobalt steels the Ni and Co are converted into complex cyanides, the cobalt cyanide is oxidised to the stable cobalti-form with  $\text{H}_2\text{O}_2$  and the Ni is pptd. with dimethylglyoxime, the nickelocyanide being decomposed selectively with formaldehyde. The filtered glyoxime is dissolved and the Ni is titrated as in the first method. The reproducibility is  $\pm 0.01$  per cent. up to 0.25 per cent. of Ni.

N. E.

**3371. Ion-exchange separation of rhodium and iridium.** E. W. Berg and W. L. Senn, jun. (*Anal. Chem.*, 1955, **27** [8], 1255-1256).—The rapid and simple procedure described is based on the anionic nature of the  $\text{Ir}^{\text{IV}}$ -thiourea complex and the cationic nature of the  $\text{Rh}^{\text{III}}$ -thiourea complex, whereby  $\text{Ir}^{\text{IV}}$  passes through a conditioned cation-exchange column (17.5 cm  $\times$  1.4 cm, Dowex 50W-X 8) whilst  $\text{Rh}^{\text{III}}$  is retained and can be eluted with 6 M HCl at 74°C. Column separation is quant., with subsequent 100 per cent. recovery of both metals as  $\text{IrCl}_4$  and  $\text{RhCl}_3$  (by dissolution of the thiourea complexes in hot 12 M HCl). W. J. BAKER

**3372. Micro-reflectivity analysis of coal.** J. T. McCartney and L. J. E. Hofer (*Anal. Chem.*, 1955, **27** [8], 1320-1325).—A quant. procedure for determining variations in reflectivity of a solid block, or granular briquette, of coal on a moving micro-spectro-stage is described in detail, and typical reflectivity distribution curves for some coals are shown and discussed. The procedure, which evaluates the percentage of the opaque, difficultly liquefiable components of coal better than the thin-section technique, can be applied to the selection of coal suitable for hydrogenation, to the control of blending of coking coal, and to the quant. petrographic classification of coal along the lines proposed by Van Krevelen. W. J. BAKER

**3373. Improved plastometer for studying agglutinating behaviour of caking coals.** G. L. Barthauer (*Anal. Chem.*, 1955, **27** [6], 969-971).—A rugged and dependable plastometer is described and illustrated for measuring the agglomerating (or agglutinating) strengths of various coals. The torque required to drive a stirrer through a carbonising bed is measured. Accurate measurements can be made on both strongly and weakly caking coals with this research and control instrument with the single torque unit of limited range, by diluting the coal with various (but standard) percentages of inert material. Graphs show some typical results and the effect of adding increasing amounts of  $\text{Na}_2\text{CO}_3$  to a bed of caking coal and diluent char. O. M. WHITTON

**3374. Simple batch analysis of glass.** L. Springer (*Glas-Email-Keramo-Tech.*, 1955, **6** [5], 153-154).—The simple separation of the water-soluble constituents by extraction with  $\text{H}_2\text{O}$  is, in fact, an extraction with an alkaline solution derived from the soda-ash of the batch. Some constituents of the batch (e.g., sand, limestone) are sufficiently soluble in the alkaline solution to introduce an appreciable error. Practical analytical figures show that in certain batches (e.g., opal glass) containing hydrated  $\text{Al}_2\text{O}_3$ , cryolite, bone-ash, or  $\text{ZnO}$ , up to 6 per cent. of these constituents may be incorrectly reported as water-soluble constituents.

J. A. SUGDEN

**3375. Systematic scheme of analysis of Siemens-Martin slags by means of photocolourimetry.** V. M. Bereznyak, V. A. Begma and V. I. Zhuravskaya (*Zavod. Lab.*, 1955, **21** [3], 298-301).—Methods of determining  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , total Fe, MnO, MgO,  $\text{P}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  by well-known photocolourimetric methods, and CaO by titration, are described.

G. S. SMITH

**3376. Spectrographic method of determining the thickness of galvanic coatings.** V. P. Borzov and E. V. Il'ina (*Zavod. Lab.*, 1955, **21** [3], 327-331).—The spectrum of the coating is obtained on a plate moving at a const. rate, and the change in the relative intensity of a pair of lines, one belonging to the coating metal and the other to the base metal, is plotted. For single-layer coatings of Cr and Ni on brass, and of Ni, Cr, Cd and Cu on steel, results for thickness calculated from standardisation graphs show errors of 7 to 8 per cent. A variation of the method suitable for two- and three-layer coatings of different metals is described.

G. S. SMITH

### 3.—ORGANIC ANALYSIS

**3377. Determination of organic nitrogen by Kjeldahl method without distillation.** C. I. Adams and G. H. Spaulding (*Anal. Chem.*, 1955, **27** [6], 1003-1004).—The method of Marcali and Rieman for the Kjeldahl determination of organic nitrogen, without distillation, based on the titration of  $\text{NH}_4^+$  with NaOH soln. in the presence of formaldehyde (*Brit. Abstr. C*, 1947, 168), has been modified so that Se may be used as a catalyst. A sample of  $(\text{NH}_4)_2\text{SO}_4$  containing 21.22 per cent. of N was analysed four times. The mean result was 21.26 per cent. of N and the mean deviation was 0.01 per cent. After digestion of the sample in the usual way, sulphurous acid was added to precipitate the Se, and excess of acid was removed by boiling for 30 min. The completeness of removal was determined by testing with dil.  $\text{KMnO}_4$  solution. To prevent the pptd. Se from redissolving on heating, a relatively large volume of water (50 ml) was added after the digestion. The optimum pH for the addition of formaldehyde was found to be 6.8 to 6.9. After the addition of formaldehyde, the pH falls to about 4.4, in 10 min.; the titration with NaOH soln. is then carried out.

O. M. WHITTON

**3378. The micro-analysis of organic fluorine compounds.** R. Belcher (*Ost. ChemZtg.*, 1954, **55** [11-12], 158-160).—The titration of  $\text{F}^-$  with thorium nitrate can give excellent results and is particularly suitable for the determination of amounts  $< 1$  mg. Alizarin S is the best indicator, but the reaction is not stoichiometric. The presence of simple electrolytes such as NaCl affects the result but can be allowed for. Quantities of 25 to 60 mg can be assayed by the gravimetric determination of lead fluorochloride. Since lead fluorobromide and fluoroiodide are more soluble,  $\text{Br}^-$  and  $\text{I}^-$  do not interfere. A direct titration, suitable for quantities of 2 to 20 mg, is possible with aluminium chloride, Eriochrome cyanine being used as indicator. In another method the pptn. of calcium fluoride and the back-titration of excess of calcium salt with EDTA (disodium salt) are used;  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{AsO}_4^{3-}$  do not interfere. The best method of decomposing the organic fluorine compound is

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fusion at 650° C with Na or K in a nickel bomb. The determination of the halogens in the presence of each other is described. P. S. STROSS

**3379. Determination of acetylenic hydrogen by means of concentrated silver solutions.** L. Barnes, jun., and L. J. Molinini (*Anal. Chem.*, 1955, **27** [6], 1025-1027).—A rapid and accurate procedure described for the acidimetric determination of acetylenic hydrogen is based on the observation that concentrated aqueous solutions of  $\text{AgNO}_3$  and  $\text{AgClO}_4$  form soluble complexes with acetylene, accompanied by a simultaneous quant. liberation of  $\text{H}^+$ . The concn. of the aqueous silver salt used as reagent is 2.0 to 3.5 *M*. The procedure has been successfully applied to acetylenic alcohols, hydrocarbons, carboxylic acids, amines, and miscellaneous compounds with an accuracy within  $\pm 5$  per cent. The principal advantages are speed of analysis, a minimum of reagents, and the absence of a ppt. of silver acetylide. Halogens and aldehydes do not interfere. The liberated acid is titrated with 0.1 *N* base to the green colour of the methyl purple indicator as viewed by transmitted light. Acidic or basic impurities and functional groups, if present, may be determined separately and appropriate corrections applied. The apparatus is illustrated and the procedure used for gaseous samples is also described. O. M. WHITTON

**3380. Micro- and semi-micro determination of alkoxy groups.** R. Belcher, J. E. Fildes and A. J. Nutton (*Anal. Chim. Acta*, 1955, **13** [1], 16-22).—After examining sources of error in the determination of alkoxy groups, a modified procedure for the semi-micro and micro-estimation of methoxyl and ethoxyl groups is given. The sample is dissolved in a soln. of phenol in propionic anhydride, and a small drop of Hg (or two or three platinum tetrahedra) is added to prevent bumping. After distillation with HI in an atm. of  $\text{CO}_2$ , the alkyl iodide vapours are washed in a 10 per cent. soln. of Na Sb tartrate and absorbed in a soln. of acetic acid and sodium acetate containing Br. Excess of Br is destroyed with formic acid, and the estimation is completed iodimetrically. A simple apparatus for the determination is described. J. H. WATON

**3381. Test for the vicinal dithiol group.** D. H. Rosenblatt and G. N. Jean (*Anal. Chem.*, 1955, **27** [6], 951-954).—The procedure for using manganous acetate, in a system containing pyridine and water, as a specific reagent for compounds containing thiol groups on adjacent carbon atoms is described. Pyridine, aq. manganous acetate solution and thiol solution are mixed in this order, and the absorbance at 490  $\text{m}\mu$  is read at 1 min. and at intervals afterwards; a blank is run simultaneously. Positive tests were obtained with 2:3-dimercapto-1-propanol (dimercaprol), ethanedithiol, propane-1:2:3-trithiol, and toluene-3:4-dithiol, whereas monothiols, e.g., propyl, isopropyl, *tert*-butyl, isoamyl and decyl mercaptans, and thiophenol, thioglycolic acid, mercaptosuccinic acid, 2-mercaptoethanol and 3-mercaptopropane-1:2-diol, and non-vicinal dithiols, e.g., 1:3-dimercapto-2-propanol, gave negative tests. Under suitable conditions, vicinal dithiols may be estimated in the presence of monothiols and non-vicinal dithiols. O. M. WHITTON

**3382. Determination of olefins by means of iodine complexes. Ultra-violet absorption method.** D. R. Long and R. W. Neuzil (*Anal. Chem.*, 1955, **27** [7], 1110-1114).—A reversible complex is formed

between olefins and iodine with max. absorption at 275  $\text{m}\mu$  for type  $\text{RCH}:\text{CH}_2$ , 290 to 295  $\text{m}\mu$  for  $\text{R}_2\text{C}:\text{CH}_2$ , 295 to 300  $\text{m}\mu$  for  $\text{RCH}:\text{CHR}$ , 317  $\text{m}\mu$  for  $\text{R}_2\text{C}:\text{CHR}$  and 337  $\text{m}\mu$  for type  $\text{R}_2\text{C}:\text{CR}_2$ . By choosing concn. of the olefin (0.03 to 0.1 mole per litre) and iodine (0.002 mole per litre) in purified isooctane so that  $\geq 5$  per cent. of complex is formed, the absorption is proportional to the product of the iodine and olefin concn. Since normal room lighting causes non-reversible reaction of iodine with the olefin, samples must be kept in the dark or the absorption must be measured as soon as possible. Saturated hydrocarbons do not interfere but aromatic hydrocarbons do. Examples of quant. analysis of prepared mixtures are given and show good agreement. E. J. H. BIRCH

**3383. Photometric detection of acetylene in aqueous liquids.** N. Henning, L. Demling and W. Pfanz (*Klin. Wochschr.*, 1955, **33** [25-26], 622-623).—An earlier method for detecting acetylene in expired breath of patients, based on the pptn. of copper acetylide from Ilosvay's soln., has been modified by carrying out the reaction in the presence of a highly viscous protective colloid, and thus delaying the precipitation. The gas to be tested is allowed to bubble slowly through a soln. composed of 85 per cent. of water containing 5 per cent. of Kollidon Bayer [a 20 per cent. soln. of highly viscous poly(vinylpyrrolidone)] and 10 per cent. of Ilosvay reagent. The resulting red colour of the suspension of copper acetylide is measured in a Lange colorimeter, using a Gibson filter; the result is expressed in terms of extinction. The suspension is stable for 70 min. Ilosvay reagent is prepared by dissolving 1 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in a small quantity of water and adding 4 ml of 20 to 21 per cent. aq.  $\text{NH}_3$  and 3 g of hydroxylamine hydrochloride; after being shaken, the soln. is made up to 50 ml with water. In well-stoppered vessels, the reagent is stable for 2 to 3 days. P. HAAS

**3384. Purification of cyclohexane.** N. A. Sörensen (*Chemist Analyst*, 1955, **44** [1], 24).—cycloHexane is stirred vigorously for  $\approx 3$  hours with 10 per cent. of its volume of a mixture (1:1) of 98 per cent.  $\text{H}_2\text{SO}_4$  and 68 per cent.  $\text{HNO}_3$ . The solvent layer is decanted, washed with water, and dried over anhyd.  $\text{Na}_2\text{SO}_4$ . Sulphur and nitro compounds are removed quant. by filtering through columns of activated alumina, and distillation is unnecessary. D. LIFF

**3385. Vanadium 8-hydroxyquinolate as a reagent for the detection of alcohols, thiols and amines.** A. J. Blair and D. A. Pantony (*Anal. Chim. Acta*, 1955, **13** [1], 1-7).—The deep blue-black soln. of the VV derivative of oxine in certain chlorohydrocarbons gives a distinctive colour change with various types of organic compound, provided that the organic compound is also sol. in the chlorohydrocarbon used. The reagent is specific for alcohols, with a colour change from black to red. With most amines the colour changes to golden yellow via green, but the reaction is not completely specific. A colour change to lemon-yellow via green is given by thiols, which may be confused with that given by certain amines. Acids turn the reagent blue. A semi-quant. determination of alcohols is possible if the optical density of the red soln. is measured at 700  $\text{m}\mu$ . J. H. WATON

**3386. Schiff reagent. Its preparation and its use in the determination of formaldehyde in cellulose acetate formal.** D. E. Kramm and C. L. Kolb

(*Anal. Chem.*, 1955, **27** [7], 1076-1079).—Investigation of the optimum sensitivity conditions of Schiff's reagent led to the following method of preparing the reagent. Rosaniline hydrochloride ( $4.5 \pm 0.005$  g) is dissolved in 1500 ml of water,  $\text{Na}_2\text{S}_2\text{O}_5$  ( $9.6 \pm 0.05$  g) is added and, after 5 to 10 min.,  $6\text{ N H}_2\text{SO}_4$  (40 ml). The mixture is set aside overnight, activated carbon (3 g) is added, and after being swirled for 45 sec. the reagent is filtered by suction, taking  $> 3$  min. The  $\text{SO}_2$  in the filtered reagent is estimated titrimetrically and adjusted if necessary to 2.8 to 4.8 millimoles of  $\text{SO}_2$  per 100 ml of reagent. The reagent is standardised by treatment with standard formaldehyde solution. The percentage transmittance is measured at  $550\text{ m}\mu$  after 2 to 2.5 hr. and compared with a blank in which water is substituted for formaldehyde. The Schiff reagent needs to be standardised only every 4 or 5 days. Twenty-five samples containing 0.01 to 0.8 per cent. of formaldehyde gave a standard deviation of  $\pm 0.021$  per cent. E. J. H. BIRCH

**3387. Non-aqueous titrations of dilute acids and bases in acrylonitrile.** M. L. Owens, jun., and R. L. Maute (*Anal. Chem.*, 1955, **27** [7], 1177-1178).—Organic acids in acrylonitrile are titrated directly with 0.02 N methanolic NaOH until 6 drops of alcoholic bromothymol blue give a sharp change from yellow to blue. Strong organic bases such as choline are titrated with 0.02 N  $\text{HClO}_4$  in dioxan to a green end-point with the same indicator. Weak organic bases (e.g., carboxylic acid salts of choline) are titrated by adding an equal vol. of glacial acetic acid, and 4 drops of crystal violet indicator, and titrating with 0.02 N  $\text{HClO}_4$  in dioxan or acetic acid to a green end-point. The end-point may be determined potentiometrically in the presence of a mixture of equal vol. of glycol and isopropanol. A precision of  $\pm 0.001$  per cent. is obtained with contents of  $\approx 0.002$  per cent. of choline in acrylonitrile. Carbon dioxide does not interfere as it does in aq. titration.

E. J. H. BIRCH

**3388. Gas-liquid partition chromatography: the separation and micro-estimation of volatile fatty acids from formic acid to dodecanoic acid.** J. H. Van de Kamer, K. W. Gerritsma and E. J. Wansink (*Biochem. J.*, 1955, **61** [1], 174-176).—A modification of the gas-liquid chromatographic method of James and Martin (*Brit. Abstr. C*, 1952, 199) is described. The temp. of the column is gradually increased from  $100^\circ$  to  $150^\circ\text{C}$ , and the volatile fatty acids from formic to dodecanoic acid are successively volatilised off the column and determined by titration. J. N. ASHLEY

**3389. Method for direct colorimetric determination of oxalic acid.** J. Bergerman and J. S. Elliot (*Anal. Chem.*, 1955, **27** [6], 1014-1015).—A method reported for the direct determination of oxalic acid is based on its reaction with indole to form a red or pink compound which conforms to Beer's law. It has so far been applied only to oxalic acid standards and to aliquots of calcium oxalate dissolved in known amounts of  $1\text{ N H}_2\text{SO}_4$ . Acetic, propionic, tartaric, citric, benzoic and uric acids, chloride ion (except in relatively high concentrations), and phosphate do not interfere. By photometric comparison of the colour developed with standards, 0.050 to 1.00 mg of oxalic acid per ml can be determined. Larger amounts may be determined by quantitative dilution. The absorbance is measured in a photometer at  $525\text{ m}\mu$ .

O. M. WHITTON

**3390. Cerimetric determination of sugars.** A. A. Forist and J. C. Speck, jun. (*Anal. Chem.*, 1955, **27** [7], 1166).—The method of Smith and Duke (*Ind. Eng. Chem., Anal.*, 1941, **13**, 558) has been modified and applied to D-xylose, D-ribose, and D-glyceraldehyde as well as to glucose. A weighed quantity of sugar is oxidised for 1 hr. (glyceraldehyde requires 4 hr.) at  $25^\circ\text{C}$  with  $0.28\text{ N Ce}(\text{ClO}_4)_4$  in  $4\text{ M HClO}_4$ . In one modification, 25 ml of  $0.18\text{ N}$  oxalic acid in  $0.1\text{ M HClO}_4$  are added and the excess is determined with  $0.03\text{ N Ce}(\text{ClO}_4)_4$  in  $\text{HClO}_4$ , with nitroferroin as indicator. In another modification, 2 drops of  $0.01\text{ M}$  osmic acid in  $0.1\text{ M H}_2\text{SO}_4$  and 15 ml of  $0.13\text{ N}$  sodium arsenite are added and the excess is titrated with  $0.01\text{ N Ce}(\text{ClO}_4)_4$  in  $\text{HClO}_4$ . Two equivalents of ceric ion are required for each carbon atom in the sugar molecule.

E. J. H. BIRCH

**3391. Analysis of monochloroacetic acid. A partition chromatographic method.** L. F. Dupé and K. Gardner (*Anal. Chim. Acta*, 1955, **13** [1], 57-63).—Dichloroacetic, chloroacetic and acetic acids in commercial chloroacetic acid are determined by partition chromatography on kieselguhr columns. The stationary phase is  $\text{N H}_2\text{SO}_4$  and the eluent a mixture of equal vol. of isopropyl ether and light petroleum (boiling range  $60^\circ$  to  $80^\circ\text{C}$ ). The fractions are titrated with  $0.01\text{ N}$  sodium methoxide under a stream of  $\text{N}_2$ . The method can be modified to enable sodium chloroacetate to be analysed. The dichloroacetate content of commercial samples tested is found to be higher than that quoted in the specifications. Trichloroacetic acid always accompanies dichloroacetic acid and is estimated by Fujiwara's reaction, whilst glycolic acid is not eluted from the column.

J. H. WATON

**3392. Studies on primary amines. III. Limiting and optimum conditions for quantitative determination by the ninhydrin method.** H. M. Perry and G. Goldstein (*J. Lab. Clin. Med.*, 1955, **45** [6], 963-972).—In the method described, the primary amine ( $0.1$  to  $0.01\text{ }\mu\text{mole}$ ) in water-free isopropanol is treated with pyridine and ninhydrin to give concn. of 50 and  $0.04$  per cent. w/w, respectively. The mixture is immediately heated for 7 min. at  $87^\circ\text{C}$  and then rapidly cooled to  $20^\circ\text{C}$ . The optical density at  $417\text{ m}\mu$  is read after 15 to 90 min. at room temp. The limiting and optimum conditions of water content, electrolyte concn. and excess of acid or base in the test soln. are studied in detail, and limits are prescribed for optimal results. Total primary aliphatic amine groups can be determined by the method, provided that they occur on unbranched and unsubstituted carbon chains; for aromatic- and heterocyclic-substituted amines the determination is less accurate, unless known standards can be used. W. H. C. SHAW

**3393. Determination of amides in aqueous and non-aqueous solution by the Conway diffusion technique.** H. E. Hallam (*Analyst*, 1955, **80**, 552-556).—A rapid method is described for the determination of amide N with an accuracy of  $\pm 0.2$  per cent., the optimum amount of sample being that equivalent to  $0.28\text{ mg}$  of N in  $1\text{ ml}$ . The base is liberated by  $1\text{ ml}$  of  $10\text{ N KOH}$  and is absorbed in  $\approx 1\text{ ml}$  of  $1.5$  per cent.  $\text{H}_3\text{BO}_3$  containing a methyl red-bromocresol green indicator. The absorbent is finally micro-titrated with  $0.02\text{ N HCl}$ . Formamide can be determined in 3 hr., or in 1 hr. 50 min. with oscillation. Acetamide needs 5 hr.,

or 3 hr. with 32 hr. owing to methylation of urethane. Difficulties aqueous solution creeping portions treated with normal necessary aqueous solution is rapid but mination of be impossible (32 hr.), cannot be described

**3394. G. sulphenyl** (*Anal. Chem.*, 1955, **27** [7], 1177-1178).—Dinitrobenzenesulphenyl benzenesulphenyl is iodine  $21^\circ \rightarrow \text{Ar}$  dried for 24 hr. in Erlenmeyer then an sulphenyl and swi 1-5 min followed added w is estim organic present, (after t carbon t the det accurate water is magnitu the oxy to obs sulphen

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or 3 hr. with oscillation. N-Methylacetamide needs 32 hr. owing to the slow rate of absorption of methylamine. The method is not applicable to urethane, the rate of hydrolysis being too low. Difficulties occurring in the determination of non-aqueous solutions are due to condensation and creeping of the solvent, even when the middle portions of the lids are greased and the edges treated with a silicone fixative; duplication of the normal number of three units per determination is necessary to allow for rejections. With non-aqueous solutions, the initial evolution of the base is rapid but in the later stages it is slower. Determination of N-methylacetamide in  $\text{CCl}_4$  appears to be impossible because, in the long absorption period (32 hr.), all units are contaminated. Amides that cannot be determined directly by the method described require previous Kjeldahl digestion.

A. O. JONES

**3394. Quantitative determination of certain sulphenyl halides.** N. Kharasch and M. M. Wald (*Anal. Chem.*, 1955, **27** [6], 996-998).—A general procedure for the quantitative estimations of 2:4-dinitrobenzenesulphenyl chloride, the corresponding sulphenyl bromide and thiocyanate, and 2-nitrobenzenesulphenyl chloride is described. The method is iodimetric and involves the reaction  $2\text{ArSCl} + 2\text{I}^- \rightarrow \text{ArSSAr} + \text{I}_2 + 2\text{Cl}^-$ . To NaI (4 to 6 g, dried for 1 hr. at  $110^\circ\text{C}$ ) in a 250-ml glass-stoppered Erlenmeyer flask, dry acetic acid (10 to 20 ml) and then an aliquot of the prepared solution of the sulphenyl halide are added. The flask is stoppered and swirled briefly three or four times during 1-5 min. Distilled water ( $\approx 120$  ml) is added, followed by an excess of standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution, added with gentle swirling. The excess of  $\text{Na}_2\text{S}_2\text{O}_3$  is estimated by back-titration with iodine. If an organic solvent of density lower than water is present, e.g., ether or benzene, it is useful to add (after the water has been introduced) sufficient carbon tetrachloride or ethylene chloride to increase the density of the organic phase. Titrations accurate to  $\pm 1$  per cent. are easily obtained when water is excluded. In anhydrous acetic acid, the magnitude of the required blank is proportional to the oxygen tension. The titration may be applied to observing the rates of reactions involving sulphenyl halides.

O. M. WHITTON

**3395. Polarographic determination of dialkyl dithiophosphates.** R. F. Makens, H. H. Vaughan and R. R. Chelberg (*Anal. Chem.*, 1955, **27** [7], 1062-1064).—A number of sodium dialkyl dithiophosphates (up to butyl) are polarographed *vs.* the S.C.E. with 0.1000 N  $\text{HClO}_4$  as base electrolyte, and a dropping-mercury or a flowing-junction platinum anode. Electrolysis with micro-electrodes serves to isolate mercuric dialkyl dithiophosphates as products from the mercury electrode and di-(OO-dialkyl dithiophosphoryl) disulphides from the platinum electrode, suggesting that the Hg takes part chemically in the reaction. The current-concn. plot for the micro-electrode is linear up to  $10^{-3}$  M. The  $E_{1/2}$  becomes increasingly more negative as the mol. wt. increases.

E. J. H. BIRCH

**3396. Infra-red characterisation of side-chain substitution of monoalkylbenzenes.** W. J. Potts, jun. (*Anal. Chem.*, 1955, **27** [6], 1027-1030).—Characterisation of substitution of the alpha position or of any higher position of monoalkylbenzenes can be made by infra-red absorption spectra. Good correlation was found to exist

between the position of substitution and the exact wavelength of the infra-red absorption intensity at  $\approx 13.3 \mu$ , which is characteristic of monoalkylbenzenes. Wavelengths of strong bands in the 13 to  $14\text{-}\mu$  region are tabulated for certain substituted monoalkylbenzenes.

O. M. WHITTON

**3397. Distillation micro-methods for the analysis of petroleum.** A. R. Javes, C. Liddell and W. H. Thomas (*Anal. Chem.*, 1955, **27** [6], 991-996).—Micro-stills (illustrated) and the procedure for the analysis of petroleum are described. Tests with micro-stills on oil samples as small as 0.8 ml gave results agreeing with those obtained by the corresponding standard methods (IP 24, IP 123 or ASTM D 86 at atmospheric pressure, or ASTM D 1160 under vacuum), but the experimental error is three times as great. Distillates and residues from 5-ml portions of crude oil cut in a micro-still having a packed column had properties agreeing with those prepared from several litres of crude oil with a large 14-plate column.

O. M. WHITTON

**3398. Rapid polarographic determination of tetraethyl-lead in gasoline.** W. Hubis and R. O. Clark (*Anal. Chem.*, 1955, **27** [6], 1009-1010).—The 2-ethoxyethanol (Cellosolve) - hydrogen chloride method for the decomposition of tetraethyl-lead and the simultaneous extraction of lead from petrol containing tetraethyl-lead is subject to limitations when the lead is determined polarographically. Study showed that if the 2-ethoxyethanol were cooled in an ice-bath during acidification with anhydrous hydrogen chloride, the residual current could be measured with more reliability; if a little gelatin solution were added the reliability of measuring both residual and diffusion currents could be improved; and if water were added to the 2-ethoxyethanol - hydrogen chloride electrolyte (I) after decomposition of the tetraethyl-lead, certain interferences encountered with aged, cracked petrols could be eliminated. The modified procedure is given.

O. M. WHITTON

**3399. Determination of trace amounts of carbonyl sulphide in gaseous hydrocarbons.** R. E. Snyder and R. O. Clark (*Anal. Chem.*, 1955, **27** [7], 1167-1171).—An apparatus is described for the preparation of COS by the interaction of sulphuric acid with  $\text{KSCN}$ , and the purification of the gas with KOH and Ascarite (short time of contact to avoid absorption of the COS). The pure COS is used to calibrate a method (apparatus described) for determining COS in non-aromatic hydrocarbon mixtures. The gas containing COS is passed over specially prepared  $\text{MnO}_2$ , which removes both  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , and is allowed to react with a solution of 0.5 g of piperidine in 1 litre of 95 per cent. ethanol. The amount of COS is measured by the absorption of the piperidine thiocarbamate formed, at  $230 \mu\mu$ . Aromatic hydrocarbons in concn.  $< 50$  p.p.m. do not interfere, and interference above this level can be allowed for.

E. J. H. BIRCH

**3400. Determination of organic sulphur compounds in a gas by converting them into hydrogen sulphide.** Ya. D. Zel'venskiĭ, A. N. Gruzintseva and S. Yu. Gerchikova (*Zavod. Lab.*, 1955, **21** [3], 277-281).—The gas, freed from  $\text{H}_2\text{S}$  by passage through an absorbent containing 185 g of  $\text{Na}_2\text{CO}_3$  and 150 g of  $\text{K}_3\text{Fe}(\text{CN})_6$  in 1 litre of water, enters a quartz tube (12 to  $15 \text{ mm} \times 80 \text{ cm}$ ), filled with pieces of quartz (3 to 5 mm in diameter) and heated in a tube furnace (50 to 60 cm in length)

to between 900° and 1100° C, at a rate of 1 to 2 litres per sec. The  $H_2S$  formed is absorbed in 100 ml of 2 per cent. cadmium acetate soln. containing 10 ml of glacial acetic acid per litre. Excess of 0.01 or 0.02 N I is added and the excess is determined by titrating with thiosulphate, with starch as indicator. With sulphur contents greater than several tenths of a mg per cu. metre, the complete determination takes 15 to 20 min. Any O in the gas becomes converted into  $H_2O$  and does not interfere. The method can be used in the absence of organic compounds containing H by mixing 25 per cent. of H with the gas.

G. S. SMITH

**3401. Colorimetric determination of N-phenyl-1-naphthylamine in new and used (lubricating) oils.** W. S. Levine and W. A. Marshall (*Anal. Chem.*, 1955, **27** [6], 1019-1022).—A rapid, colorimetric method is described for determining N-phenyl-1-naphthylamine, an oxidation inhibitor, in new and used industrial oils. The oil is dissolved in acetone and diazotised *p*-nitroaniline is added to produce a blue-violet colour. A single determination takes 18 to 20 min. The accuracy is within  $\pm 10$  per cent., which is adequate for blending-plant control work and routine analysis. In the qualitative test, 10 ml of acetone are added to 2 or 3 drops of the oil sample in a crucible and the mixture is stirred for 30 sec. A drop of the diazotised *p*-nitroaniline is added and stirred in. A bluish-purple colour that increases rapidly indicates that N-phenyl-1-naphthylamine is present in the oil. A quantitative method is also described.

O. M. WHITTON

**3402. The colloid chemical analysis of coal tar.** H. Mallison (*Bitumen, Teere, Asphalte, Peche*, 1955, **6** [6], 195).—In the determination of coal-tar constituents soluble in various solvents, it has been found convenient to use a IG4 sintered-glass crucible containing a 1-cm layer of powdered glass. The layer is moistened with benzene, pressed down, sucked "dry" and dried before use. In cleaning, the glass is easily removed, carrying the insoluble matter with it, and the sintered glass is not blocked.

A. B. DENSHAM

**3403. Chromatographic method for the fractionation of asphalt into distinctive groups of components.** L. R. Kleinschmidt (*J. Res. Nat. Bur. Stand.*, 1955, **54** [3], 163-166).—In a chromatographic method for separating asphalt into four distinctive groups of components, a column of fuller's earth is used as adsorbent, and *n*-pentane, methyl chloride and ethyl methyl ketone are employed as selective solvents. This fractionation facilitates chemical studies of the degradation of asphalts under service conditions. The method is well suited to samples as small as those used in conventional weathering and accelerated durability tests, i.e., about 5 g. With this sample weight, the time required for complete fractionation is 6 to 8 hr., according to the nature of the asphalt, and the time required to fractionate the components soluble in *n*-pentane is about 3 hr.

C. J. KEATCHE

**3404. The estimation of fluorescein in dilute solutions.** E. Shotton and A. F. S. A. Habeeb (*J. Pharm. Pharmacol.*, 1955, **7** [7], 456-462).—Fluorescein may be determined with an error of  $< 6$  per cent. in the concn. range 0.02 to 1.5  $\mu$ g per ml, and detected down to a concn. of 0.001  $\mu$ g per ml, by measurement of the fluorescence in an aq. buffer of pH 6, using a Chance filter OG1. The fluorescence of an aq. soln. is unaffected by exposure

to diffused daylight at room temp. for 14 days, or by boiling under reflux for 8 hr. (or 80 hr. for a 0.1 per cent. soln.).

A. R. ROGERS

**3405. Dilution paper-chromatography and its application to the examination of phenol-formaldehyde resins.** (Preliminary communication.) E. Zichy (*Magyar Kém. Foly.*, 1955, **61** [3], 91-92).—Acetone is used as eluent in the ascending method and, by diluting it continuously with  $H_2O$ , two fractions can be distinguished in phenol-formaldehyde resins. One has  $R_F = 0$  at a characteristic concn. of  $H_2O$ ; this spot can be detected with diazotised sulphanilic acid. The critical concn. are characteristic of the various types of resins. The other fraction has a fairly constant  $R_F$  (0.7 to 0.8) and can be detected with  $AgNO_3$ -aq.  $NH_3$  soln.

A. G. PETO

**3406. Routine exchange-capacity determinations of ion-exchange resins.** S. Fisher and R. Kunin (*Anal. Chem.*, 1955, **27** [7], 1191-1194).—Methods for the determination of both anion- and cation-exchange capacities of ion-exchange polymers have been devised. For cation-exchange capacity the no. of groups capable of exchanging cations is determined by converting the resin groups to the H form with excess of acid, washing out the excess and equilibrating the resin with a known excess of 0.1 N NaOH in 5 per cent. aq. NaCl. The excess is titrated with 0.1 N acid. For anion-exchange capacity the resin is converted to the OH form and equilibrated with acid in a similar way. The effect of the initial ionic form of the resin on the measured capacity has been investigated.

W. J. BAKER

**3407. Analysis and testing [of paints].** Anon. (*Paint Manuf.*, 1955, **25** [6], 234-235).—Recently published methods for the analysis and testing of pigments, infra-red spectrophotometry, measurement of paint-film thickness and hardness, testing of colour-matching ability, analysis and testing of resins, testing of the fire hazards of painted surfaces and the testing of the general performance and mould-growth resistance of paints are reviewed. (17 references.)

D. R. DUNCAN

**3408. Determination of the non-volatiles content of paint media.** Oil and Colour Chemists' Association, Manchester Section (*J. Oil Col. Chem. Ass.*, 1955, **38** [7], 362-365).—A standard method, based on the loss of weight of a sample during oven-drying, has been formulated by the Manchester Section, O.C.C.A., after co-operative investigation by several laboratories. The sample ( $2.5 \pm 0.5$  g) is dried in a previously tared Petri dish (3 in. in diameter) with a lid; the drying both for tare and sample is at  $110^\circ \pm 2^\circ$  C. Not more than four dishes should be in the oven together and care must be taken to minimise solvent evaporation during transference of sample to dish.

S. C. I. ABSTR.

**3409. Polarographic determination of nitroglycerin in double-base powder.** G. C. Whitnack, M. M. Mayfield and E. St. Clair Gantz (*Anal. Chem.*, 1955, **27** [6], 899-901).—A rapid and reliable method for the extraction and polarographic analysis of nitroglycerin from double-base powder (a powder containing both nitroglycerin and cellulose nitrate) is described. A weighed sample (0.5 to 1.0 g) of the microtomed or Wiley-milled powder is refluxed with 50 ml of 95 per cent. ethanol for 30 min. and then filtered through a No. 41 Whatman filter-paper. The flask and filter are washed with 95 per

cent. ethanol. An aliquot of 95 per cent. 15 ml (usual cent. ethanol-chloride so nitrogen constant graphic work the average standard and phth nitrodiphenyl compound applied. value of the ammonium the S.C.E. a precision

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cent. ethanol, and the filtrate is made up to 100 ml. An aliquot of the diluted extract is added to 95 per cent. ethanol so that the final volume is 15 ml (usually a 5-ml aliquot and 10 ml of 95 per cent. ethanol); 5 ml of 0.1 M tetramethylammonium chloride solution are then added. During analysis, nitrogen is passed through the solution kept at constant temp. A polarogram of the solution is obtained from 0.0 to -1.60 V. Duplicate polarographic waves are produced for the solution, and the average wave-height in mm is referred to a standard graph for nitroglycerin. Cellulose nitrate and phthalic acid esters do not interfere. If 2-nitrodiphenylamine, dinitrotoluene, or other nitro compounds are present, a small correction must be applied. The diffusion current is a linear function of the concentration of nitroglycerin. The  $E_{1/2}$  value of nitroglycerin in 0.5 M tetramethylammonium chloride (in 75 per cent. ethanol), vs. the S.C.E., is -0.70 V. The data obtained have a precision of about  $\pm 0.9$  per cent.

O. M. WHITTON

**3410. Test for establishing residual safe-life of stabilised solid propellants.** C. Boyars and W. G. Gough (*Anal. Chem.*, 1955, **27** [6], 957-961).—A test is described for measuring the stabiliser loss in propellants in terms of the proportion of original safe-life remaining, and its evaluation in propellants subjected to varying periods of high-temperature storage, e.g., those with a cellulose nitrate-nitroglycerin base, and containing either 1 per cent. of sym-diethyldiphenylurea or 2 per cent. of 2-nitrodiphenylamine as stabiliser. This stability test involves heating the volatile-free propellant at constant temperature in a constant-volume system containing an oxygen atmosphere. The time required to reach a predetermined positive pressure correlates well with residual safe-life as measured by the length of preliminary storage of the propellant at high temperature. Data are presented comparing the variation of pressure with time in tests carried out under atmospheres of nitrogen, air and oxygen. Hypotheses on the mechanism of degradation of propellants, based on this work, are offered.

O. M. WHITTON

**3411. Amperometric titrations of organic compounds.** N. Konopik (*Öst. ChemZtg*, 1954, **55** [9-10], 127-137).—Applications of metal salt solutions (cf. *Öst. ChemZtg*, 1953, **54**, 289, 325) to amperometric determinations of organic compounds are described. They include many types of organic compounds, among which are aromatic amines and diamidines, acridine derivatives, streptomycin, phenols, alkaloids, barbiturates, terpenes, ascorbic acid,  $\alpha$ -tocopherol, mercaptans, mercaptobenzothiazole, thiourea, phenazone and diphenylhydantoin (phenytoin).

D. R. GLASSON

**3412. Determination of organic substances by standard chromous chloride solution.** R. S. Bottei and N. H. Furman (*Anal. Chem.*, 1955, **27** [7], 1182-1184).—Chromous chloride (0.1 N) in 0.1 N HCl, prepared according to Lingane and Pecsok (*Brit. Abstr. C*, 1948, 230), is used for the direct and indirect (by back-titration with ferric alum) titration of reducible organic substances. Results are given for o-nitro- and 2:4:6-trinitro-benzoic acid, 2:4:6-trinitroresorcinol, 2:4-dinitrophenylhydrazine, nitroguanidine, p-nitrophenylazoresorcinol, nitroso-R salt, monopotassium salt of acetylenedicarboxylic acid, and disodium anthraquinone-2:7-sulphonate. The end-point is indicated potentiometrically, but as Pt catalyses the interaction of  $H^+$  with  $Cr^{++}$  the

electrode is not lowered into the solution until it is required. For the back-titration, 200 to 250 per cent. excess is usually sufficient. With disodium anthraquinone-2:7-sulphonate the back-titration cannot be used, as the reduction product reacts with  $Fe^{+++}$ . In some cases the reduction with  $Cr^{++}$  must be carried out at elevated temp. and the vessel is then surrounded with a beaker wound with asbestos-covered heating wire.

E. J. H. BIRCH

See also Abstracts 3243, 3341, 3422.

#### 4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

**3413. Some examples of the application of partition chromatography in biological chemistry.** P. Boulanger (*Chim. Anal.*, 1955, **37** [7], 227-240).—A short account of partition chromatography is given, and it is mentioned that the technique generally gives poor results with high-mol.-wt. compounds such as proteins. Some examples of the use of partition chromatography in biological chemistry are given. These comprise the identification of an unknown substance in urine, the determination of the structure of a polypeptide, the investigation of the enzymatic deamination of an amine, and the separation and identification of polysides in human milk.

J. H. WATON

**3414. Micro-method for continuous and simultaneous determination of carbon dioxide and of oxygen by means of a modified Warburg apparatus.** L. Chapon (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 171-180).—See *Anal. Abstr.*, 1955, **2**, 2821.

**3415. Application to biological media of the electrochemical method for the measurement of oxygen, and its performance.** K. Damaschke, L. Rothbühr and F. Tödt (*Biochem. Z.*, 1955, **326** [6], 424-432).—Experiments with the electrochemical method for the estimation of oxygen (Tödt, Leschber and Tarnow, *Z. Naturforsch.*, 1954, **9b**, 743) are reported. The design of several forms of the apparatus is given and its application to problems of photosynthesis is discussed.

G. W. CAMBRIDGE

**3416. The concentration of potassium in glomerular urine of *Necturi*. [Determination of potassium.] P. A. Bott (*J. Biol. Chem.*, 1955, **215** [1], 287-293).—A colorimetric ultramicro-method is described for the determination of K. It depends on the pptn. of K as Na K cobaltinitrite in a capillary U-tube, and photo-electric determination of the nitrite in the ppt. by use of the colour reaction with a mixture of benzidine and 1-naphthylamine. With only 0.2  $\mu$ l of liquid, containing 0.027 to 0.078  $\mu$ g of K, the average error is  $\approx 3.6$  per cent.**

J. N. ASHLEY

**3417. Spectrophotometric determination of serum copper with bis-cyclohexanone oxalylidihydrazone.** R. E. Peterson and M. E. Bollier (*Anal. Chem.*, 1955, **27** [7], 1195-1196).—To 1 ml of heparinised serum is added 0.7 ml of 2 N HCl and, after 5 to 10 min., 1 ml of 20 per cent. trichloroacetic acid, and the liquid is centrifuged at 3000 r.p.m. for 30 min. The supernatant liquid (2 ml) is adjusted to between pH 7.5 and 7.9, and 0.2 ml of a saturated solution of bis-cyclohexanone oxalylidihydrazone in 50 per cent. ethanol is added and the absorption measured.

The molar absorption at 600  $\mu$  is 16,000 (greater than that of the more usual colorimetric reagents for Cu), and the colour is stable at room temp. for 60 min. The complex obeys Beer's law up to 4 p.p.m. of Cu. For each mole of Cu, 8 moles of reagent are required. Lead, Zn and Ni interfere at a concn. of 0.5 p.p.m. The interference of Fe (if < 10 p.p.m.) is suppressed by citrate, which does not interfere below 3000 p.p.m.;  $\text{CN}^-$  interferes in concn. of < 0.1 p.p.m. E. J. H. BIRCH

**3418. An improved method for the spectrochemical determination of zinc in blood.** N. W. H. Addink (*Rec. Trav. Chim. Pays-Bas*, 1955, **74** [3], 197-205).—The spectrochemical method described for determining Zn in blood gives results with a standard deviation of  $\pm 5$  per cent. The metal is completely volatilised from a rotating anode from a weighed amount (10 mg) of blood ash. The constant arc-temperature is made independent of the varying sodium content of the blood ash by adding 1 mg of NaCl to 10 mg of ash. For the absolute concentration of Zn in various blood samples, values found in applying the method of successive additions agreed satisfactorily with those determined chemically. O. M. WHITTON

**3419. The absorptiometric determination of mercury in urine.** A. C. Rolfe, F. R. Russell and N. T. Wilkinson (*Analyst*, 1955, **80**, 523-530).—A rapid method is described for the absorptiometric determination of Hg in urine. The urine is oxidised with  $\text{HNO}_3$  and  $\text{KMnO}_4$  in a bottle adequately stoppered to withstand pressure, and immersed in a beaker of water heated in a bath of boiling water. After the oxidation,  $\text{KMnO}_4$  is added, if necessary, until an excess is still present after 2 min. The excess is then removed by the addition of ammoniacal hydroxylamine soln. (purification described). The soln. is made alkaline with aq.  $\text{NH}_3$ , treated with dil.  $\text{H}_2\text{SO}_4$  and ammoniacal hydroxylamine soln., diluted to a definite vol. and set aside for at least 3 hr. An aliquot portion is then extracted with a soln. of dithizone in toluene and the extract is purified by extraction with dil. HCl and re-extraction with the dithizone soln. Excess of dithizone is removed by extraction with dil. NaOH soln. and the soln. of mercury dithizonate in toluene is filtered. Its optical density is then determined with a Spekker absorptiometer, with Calorex H503 and Ilford No. 602 filters, against toluene, and the mercury content is ascertained from a calibration graph prepared with standard  $\text{HgSO}_4$  solutions subjected to the same extraction procedure. The method gives complete recovery even with samples that have been standing for several days.

A. O. JONES

**3420. Rapid micro-procedure for the determination of mercury in biological and mineral materials.** D. Polley and V. L. Miller (*Anal. Chem.*, 1955, **27** [7], 1162-1164).—The Hg in a sample digested with  $\text{H}_2\text{SO}_4$  - 50 per cent.  $\text{H}_2\text{O}_2$  in the presence of  $\text{Cl}^-$  is treated with a solution of diaryl Hg to form two mol. of the corresponding org. mercury compound, which is estimated colorimetrically with dithizone. Samples are digested with conc.  $\text{H}_2\text{SO}_4$  in a flask fitted with a condenser, until the solution becomes white or pale yellow. Slight variations in this method are required for samples containing much organic matter or water. Potassium permanganate is added to the cooled diluted digest until an excess remains, which is removed with hydroxylamine hydrochloride. The mixture is filtered, N NaCl being used for the transfer, and made up to 100 ml.

An aliquot of the digest containing 0 to 8  $\mu\text{g}$  or 17 to 27  $\mu\text{g}$  of Hg is diluted in a separating funnel and buffered with 4 N sodium acetate to pH 3 to 4. One ml (or 2 ml for the higher range) of di-*p*-tolylmercury solution (20 mg in 200 ml of ethanol) is added, and the solution is extracted with  $\text{CHCl}_3$  (9.5 ml). The  $\text{CHCl}_3$  phase is transferred to a separating funnel containing 25 ml of 0.3 N acetic acid. One ml of a solution containing sufficient dithizone for the expected content of Hg is added and the complex is determined colorimetrically at 620  $\mu$ . The possibility of adsorption of Hg by the glass in these circumstances is investigated. The recovery by this method is illustrated for several soils, fish meal, bulb husks, bulb tissue, wheat kernels and air-analysis solution. No interference is caused by 1 mg of Fe, Co, Ni, Zn, Cd, Pb, Fe, Cu, Mn or Bi. If Ag is present a further shaking of the  $\text{CHCl}_3$  phase with N NaCl is necessary.

E. J. H. BIRCH

**3421. Determination of lead in urine.** W. M. McCord and J. W. Zemp (*Anal. Chem.*, 1955, **27** [7], 1171-1172).—The urine sample (100 ml) is refluxed for 20 min. with conc.  $\text{HNO}_3$  (10 ml), extracted 3 times with ether, and the ether layers are discarded. Saturated KI solution (10 ml) is added and the solution is extracted 3 times with 10-ml portions of methyl isopropyl ketone (saturated with 5 per cent. HCl). These are combined and extracted with 50 ml of 0.5 per cent. NaOH soln. After discarding the ketone layer the pH is adjusted to 9.5 to 10 and 10 ml of 5 per cent. ammonium citrate soln. and 10 ml of 2 per cent. NaCN soln. are added. The resulting solution is shaken with several 20-ml portions of dithizone in  $\text{CHCl}_3$  (25 mg per litre). The Pb dithizonate is extracted with buffer at pH 3.4 and to the separated extract ammoniacal sodium cyanide solution is added to bring the pH to 11.5. Dithizone in  $\text{CHCl}_3$  extracts the Pb dithizonate and the absorption is measured at 510  $\mu$ . By this method, the time for analysis is reduced to 45 min. In the presence of cyanide only  $\text{Sn}^{++}$ , Tl and Bi interfere, of which only the last is usually present; methods of removing it are suggested. The recovery of added Pb is good.

E. J. H. BIRCH

**3422. Determination of organic sulphur in non-volatile materials by rapid open-tube oxidation.** E. W. McChesney and W. F. Banks, jun. (*Anal. Chem.*, 1955, **27** [6], 987-990).—The organic compound (50 to 100 mg) is digested with  $\text{HClO}_4$  (10 ml of 28 per cent. aqueous solution) in a semi-closed system at about 120° C, using  $\text{Fe}^{+++}$  as a catalyst, after which the  $\text{HClO}_4$  is decomposed by raising the temperature to between 170° and 180° C. The  $\text{HClO}_4$  that remains is dissolved in about 10 ml of water and is precipitated as the potassium salt. Sulphate is then precipitated with an exactly measured amount of  $\text{BaCl}_2$  solution, and the excess of barium is determined colorimetrically by precipitating with ammoniacal chromate, the amount of chromate remaining in solution being a measure of the S originally present. Quantities of 1 mg of S are generally determinable with an accuracy and precision of  $\pm 2$  per cent. The method may be applied to biological materials such as plasma, urine, bile and tissue. For materials of high protein and low sulphur content, the method is accurate, but the precision is not always as satisfactory as with most organic compounds. Materials containing groups especially resistant to oxidation, such as methionine, require a longer oxidation, at a temperature above 200° C. O. M. WHITTON

3423. I samples of H. J. Cal 27 [6]. described various paper str ashing of  $\text{Cr}^{III}$  to C of the C diphenyl per cent samples ing from tions for  $\pm 0.02$  to per perso

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3425. estimatio and U. 666-668). mining b composi extracti The bile Johnston 439); pu acetate (Biochem with eth the  $\text{Ca}(\text{H}_2\text{SO}_4)_2$  390  $\mu$ m standard cholic a method

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**3423. Micro-determination of chromium in small samples of various biological media.** C. H. Grogan, H. J. Cahnmann and E. Lethco (*Anal. Chem.*, 1955, **27** [6], 983-986).—A rapid routine method is described for the micro-assay of chromium in various buffers, protein solutions, plasma, sera, paper strips and urine. It consists in wet or dry ashing of the sample, hypobromite oxidation of  $\text{Cr}^{\text{III}}$  to  $\text{Cr}^{\text{VI}}$ , and spectrophotometric determination of the  $\text{Cr}^{\text{VI}}$  as its red-violet complex with sym-diphenylcarbazide. Recoveries were generally 95 per cent. or better under various conditions on samples ranging in size from 10  $\mu\text{l}$  to 10 ml containing from 0.1 to 5  $\mu\text{g}$  of Cr. The standard deviations for the procedures were all within the range  $\pm 0.02$  to 0.06  $\mu\text{g}$ . Up to 60 samples can be assayed per person per day. O. M. WHITTON

**3424. Precise determination of chloride in plasma by differential potentiometric titration.** V. P. Dole and N. A. Thorn (*Anal. Chem.*, 1955, **27** [7], 1184-1186).—The differential electrode pair consists of two Pt electrodes plated with Ag and AgCl, one of which is surrounded by a weighted glass sleeve with a rubber tip which isolates the solution near one electrode mechanically but not electrically. To 1 ml of  $\text{N H}_2\text{SO}_4$  and 1 ml of serum are added 1 ml of 0.095 N  $\text{AgNO}_3$  and the titration is completed in 0.01-ml increments with accurately diluted  $\text{AgNO}_3$  solution. Results obtained are comparable with those from ashed plasma. E. J. H. BIRCH

**3425. Critical examination of methods for the estimation of bile acids in serum.** W. Koransky and U. Thiele (*Klin. Wochschr.*, 1955, **33** [27-28], 666-668).—Various published methods for determining bile acids in serum were investigated and a composite method incorporating the best means of extraction, purification and evaluation was evolved. The bile acids are extracted by the method of Irvin, Johnston and Kopala (*J. Biol. Chem.*, 1944, **153**, 439); purified by absorption on  $\text{Ca(OH)}_2$  from ethyl acetate soln., with the procedure of Minibek (*Biochem. Z.*, 1938, **297**, 29), but washing only once with ethyl acetate; and evaluated by neutralising the  $\text{Ca(OH)}_2$  with acetic acid, dissolving in conc.  $\text{H}_2\text{SO}_4$  at 0° C and measuring the u.v. absorption at 390 m $\mu$  (Jenke, *Klin. Wochschr.*, 1939, **317**). A standard curve was prepared from soln. of pure cholic acid in conc.  $\text{H}_2\text{SO}_4$ . Recovery by this method averaged 86 per cent.

H. F. W. KIRKPATRICK

**3426. Comparative study of several methods of estimating salicylic acid in blood serum.** G. Barbezat (*Anal. Chim. Acta*, 1955, **13** [1], 83-88).—Benger's colorimetric method for estimating salicylic acid in blood serum is modified by buffering the soln. at pH 2.5 and by removing excess of tungstate with enough  $\text{Fe}^{\text{III}}$  soln. added before deproteinising. The method, however, is then slow and is sensitive to various personal factors. A simpler method consists in extracting the salicylic acid from the serum with dichloroethylene, from which it is re-extracted with an aq.  $\text{Fe}^{\text{III}}$  soln.

J. H. WATON

**3427. Microscopic identification of microgram quantities of D-fructose. Direct synthesis of crystalline 2,4-dinitrophenylhydrazone by solvent diffusion technique.** L. M. White and G. E. Secor (*Anal. Chem.*, 1955, **27** [6], 1016-1018).—A simple test is described for identifying as little as 0.5  $\mu\text{g}$  of pure or 10  $\mu\text{g}$  of chromatographically separated D-fructose by direct synthesis and microscopic

observation of crystalline D-fructose 2:4-dinitrophenylhydrazone dioxan solvate (the product from the interaction of the sugar with 2:4-dinitrophenylhydrazine in the presence of acidified dioxan). Less sensitive tests are also given by L-fucose, D-galactose, D-mannose and L-arabinose. Other common pentoses, hexoses and reducing disaccharides do not give a characteristic 2:4-dinitrophenylhydrazone under the conditions described. All of the reacting sugars can be reliably distinguished from one another by the characteristic appearance and properties of their 2:4-dinitrophenylhydrazones. O. M. WHITTON

**3428. Spectrophotometric method for the determination of 5-keto(oxo)-D-gluconic acid.** D. Perlman (*J. Biol. Chem.*, 1955, **215** [1], 353-356).—A micro-method for the determination of 5-oxo-D-gluconic acid is described. It is based on reduction of the molybdoarsenate reagent (Nelson, *Brit. Abstr. C*, 1944, **191**) at 50° C for 2 hr., and determination of the colour intensity in a photo-electric colorimeter at 660 m $\mu$ . The amount of acid is then ascertained from a standard graph. By this method, 5  $\mu\text{g}$  of the acid in fermentation samples can be determined. Fructose and sucrose have only  $\approx 8$  and 3 per cent., respectively, of the reducing power of the acid. If large amounts of these sugars are present, the sample should be passed through a column of the anion-exchange resin Amberlite IRA-400, which retains the acid; it is then eluted with 0.08 N  $\text{H}_2\text{SO}_4$  and determined as described above. The method can also be used for the determination of 2-oxo-D-gluconic acid. Under the conditions given it has  $\approx 16$  per cent. of the reducing power of the 5-oxo acid, and the method is as accurate as, and less laborious and more sensitive than, that described by Stubbs *et al.* (*Brit. Abstr. Biol.*, 1941, **44**).

J. N. ASHLEY

**3429. A simple colorimetric method for inulin estimation in kidney-clearance studies on non-diabetic and diabetic patients.** J. Führ, J. Kaczmarczyk and C.-D. Krüttgen (*Klin. Wochschr.*, 1955, **33** [29-30], 729-730).—The method is based on the reaction between anthrone and carbohydrates. The blue-green colour produced by inulin on being warmed to 55° C for 10 min. is much more intense than that given with glucose. *Procedure*—Deproteinise serum or blood (0.2 ml) with 4 per cent. trichloroacetic acid (1.8 ml). Dilute urine 10 to 100 times and treat 1 ml with 9 ml of trichloroacetic acid. Centrifuge or filter off the ppt. Layer 0.5 ml of filtrate on 5 ml of anthrone reagent [0.2 g of anthrone dissolved in 100 ml of dilute  $\text{H}_2\text{SO}_4$  (2.5:1)] in a flask with a ground-glass stopper. Stopper the flask, shake vigorously and place in a water bath at 55° C for 10 min. Use filtrates of normal blood and morning urine for comparison. The extinction at 578 m $\mu$  obeys the Beer-Lambert law. The concn. of inulin in mg per cent. is given by the extinction  $\times 125$ . For the blood and urine of diabetics, of which the glucose content may vary considerably, return the reaction mixture to the flask and keep at 100° C for a further 10 min. to develop fully the glucose colour. Multiply the difference between extinction values obtained by heating at 55° C and 100° C by 0.0369 and subtract the product from the extinction value at 55° C. This result  $\times 125$  gives the inulin concn. in mg per cent. No results are given and there is no indication of the accuracy of the method.

W. H. PARR

**3430. The carbohydrate of collagen.** J. A. Moss (*Biochem. J.*, 1955, **61** [1], 151-153).—Methods for the determination of sugars in protein hydrolysates are discussed, and it is shown that the direct determination of reducing sugars and hexosamine in collagen hydrolysates gives misleading results. Hexoses and hexosamines can be separated (and then determined by standard methods) from other protein hydrolytic products by the use of a column of Dowex 50 for isolation of hexosamine, and by using a column of Dowex 50 treated with 0.05 N HCl for isolation of the hexoses. J. N. ASHLEY

**3431. The participation of adrenaline and its derivatives in the specific dynamic action of proteins in man. [Determination of catechol amines in urine.]** I. Abelin and M. Goldstein (*Biochem. Z.*, 1955, **327** [1], 72-84).—Catechol is removed by extraction of the conc. urine with peroxide-free ether. Three extractions with *n*-butanol containing *o*-nitrobenzoic acid (1.5 g per 100 ml) remove the bulk of the catechol amines; the remainder is removed from the acidified soln. with *n*-butanol. The catechol amines are adsorbed at pH 8.2 on  $Al_2O_3$  from which they are eluted with 0.25 N HCl. The eluate is treated with ethylenediamine hydrochloride and heated to 50°C (at pH 10.4) for 20 min. After addition of NaCl, the liquid is extracted with *iso*-butanol and the fluorescence is measured at 580 and 450 m $\mu$ . Hence the adrenaline and noradrenaline are calculated. G. W. CAMBRIDGE

**3432. One-phase solvent mixtures for the separation of amino acids.** T. L. Hardy, D. O. Holland and J. H. C. Nayler (*Anal. Chem.*, 1955, **27** [6], 971-974).—The  $R_F$  values on filter-paper of arginine, lysine, aspartic acid, glutamic acid, cystine, alanine, histidine, serine, valine, phenylalanine, proline, hydroxyproline, methionine, threonine, tyrosine, glycine, leucine, isoleucine, tryptophan, norleucine, cysteic acid and cysteine have been determined by using 55 different one-phase solvent mixtures. A system for selecting promising pairs of solvents for separating particular amino acids has been based on the observation, that when a solvent was allowed to run 13 or 14 in. down the paper, two amino acids whose  $R_F$  values (expressed as percentages) differed by 5 or more were usually separated into discrete spots. Moreover, techniques have been developed for rapidly identifying 16 of a mixture of 18 amino acids on a single two-dimensional chromatogram. Alternatively, all 18 amino acids may be characterised on four separate one-dimensional chromatograms. Treatment of the chromatograms with cyclohexylamine or dicyclohexylamine before development with ninhydrin brings about striking variations in the usual colours and facilitates identification of individual amino acids, while closely related amides and peptides have been found to give colours which differ from those obtained with the parent amino acids.

O. M. WHITTON

**3433. Quantitative estimation of amino acids by circular-paper chromatography.** N. A. N. Rao and T. K. Wadhvani (*J. Indian Inst. Sci., A*, 1955, **37** [2], 130-140).—A circular-paper chromatographic method is described for the separation and estimation of amino acids. The accuracy of the method is illustrated by the analysis of edestin and bovine serum albumin, and its limitations and advantages are indicated. O. M. WHITTON

**3434. A new technique for the simultaneous microbiological determination of the essential amino acids, and conditions for their extraction in the presence of sugars.** J. Adrian (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 107-121).—Although the microbiological methods of determining the individual essential amino acids are entirely satisfactory, an attempt has been made to devise a method for their simultaneous determination. Means are described for standardising the methods of analysis by providing a medium that, with occasional slight modification, is sensibly the same for all cases. A description is given of the preparation of various solutions of vitamins, amino acids, uracil and purine bases, and their testing with *Streptococcus faecalis* and *Leuconostoc mesenteroides*, which were found to be the most suitable micro-organisms. Detailed descriptions of methods of hydrolysis of proteins are provided and of the quant. extraction of the constituent amino acids. Precautions to be taken to prevent destruction of individual amino acids, such as the use of tin for protecting lysine, are described. Results of the analyses of the 11 essential amino acids contained in various species of *Sorghum* (millet), *Pennisetum* and *Coix* (*lachryma* (Job's tears) are recorded; the very low content in tryptophan of the last-named cereal renders it unsuitable as a protein food, whilst the first two are approx. equivalent to wheat in protein value. P. HAAS

**3435. The quantitative determination of DNP [dinitrophenyl] amino acids.** G. Zimmermann (*Chem. Tech., Berlin*, 1954, **6** [5], 260-261).—Further experimental details are given of a method described earlier (*Brit. Abstr. C*, 1953, 168). It is based on the photometric measurement of the pink colour produced when the dinitrophenyl derivatives of amino acids are dissolved in alkaline acetone. The full colour is developed after 30 min. The derivatives of alanine, serine, valine and leucine give approximately similar calibration curves over a range of 25 to 250  $\mu$ g; those of proline and arginine show considerably less extinction over the same range. In no case is Beer's law obeyed completely. K. J. GARDNER

**3436. Micro-determination of  $\alpha$ -amino acids and of simple peptides by means of their complex copper salts.** P. Baudet and E. Cherbuliez (*Helv. Chim. Acta*, 1955, **38** [3], 841-847).—For quant. serial determination of  $\alpha$ -amino acids and oligopeptides, based on the formation of their cupric complexes, a cation-exchange resin (Dowex 50) containing cupric and phosphoric ions, probably as basic cupric phosphate, is described. The amount of solubilised copper is determined by colorimetric analysis of the iodine liberated on addition of iodide. A min. amount of 0.03 micro-equiv. of copper in 2 ml of soln. (the max. vol. which can be used for each analysis) can be determined. This corresponds to a concn. of 0.20  $\mu$ g of  $\alpha$ -amino nitrogen per ml for an oligopeptide, and of 0.10  $\mu$ g for an amino acid. P. HAAS

**3437. A new quantitative chromatographic determination of various amino acids in protein hydrolysates by the gradient-elution analysis principle.** T. H. J. Huisman and P. C. van der Schaaf (*Chem. Weekbl.*, 1954, **51** [1], 2-6).—The amino acids in a protein hydrolysate are separated by passing the hydrolysate down a column (150 cm  $\times$  0.9 cm) of Zeo-Karb 225 and eluting with Na citrate buffer soln. of gradually increasing ionic strength and

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hydrogen-ion concn. The column is fed with eluent from a reservoir, via a mixer; the temp. is maintained at 37° C. Aspartic acid, threonine and serine are eluted with a sodium citrate-citric acid buffer soln. of pH 3.1 and sodium concn. 0.2 M; stronger buffer soln. (pH 5.5; sodium concn. 2.0 M) is then passed into the mixer from the reservoir and the eluent passing down the column gradually increases in ionic strength and pH. After lysine has emerged from the column, the temp. is raised to 75° C to facilitate the elution of arginine. With the exception of serine and threonine, which tend to overlap, all the amino acids are clearly separated. In the determination of lysine by means of ninhydrin, variations in the strength of the citrate buffer soln. do not affect the results. Highly reproducible results are obtained in the determination of blood amino-acids, and even the amino acids present in only small amounts can be determined with great precision.

E. HAYES

**3438. A colorimetric method for the detection of amino acids, peptides and proteins on paper chromatograms and paper electropherograms.** F. Reindel and W. Hoppe (*Chem. Ber.*, 1954, **87** [8], 1103-1107).—By treatment with chlorine, liberated from HCl and  $\text{KMnO}_4$  under controlled conditions, amino acids, peptides and proteins on paper chromatograms and paper electropherograms are converted into chloramine derivatives, which give blue colours with *o*-tolidine or benzidine in acetic acid soln. in the presence of KI. By this reaction concn. of amino compounds  $< 0.0001 M$  can be detected.

A. R. ROGERS

**3439. A critical examination of various methods for glycine estimation.** H. Winter (*Z. Lebensmitt.-Untersuch.*, 1954, **99** [1], 34-42).—Methods of estimating glycine, based on its reactions with *o*-phthalaldehyde, ninhydrin followed by chromotropic acid, and fluorodinitrobenzene, are examined. The first method is considered the most suitable, but the adsorption of interfering amino acids on Wofatit is advocated. *Procedure*.—Pass 10 ml of tryptophan-free protein hydrolysate, or standard glycine soln. (5 mg per ml), through a column (20 cm  $\times$  1 cm) containing activated Wofatit to a depth of 2 cm and collect the eluate and water washings in a 100-ml calibrated flask, then make up to the mark with water. To 1 ml of the soln. add 0.5 ml of phosphate buffer (pH 8.0) and 1.5 ml of phthalaldehyde soln. (1 per cent. in 10 per cent. alcohol) and shake for 2 min. Then add 2 ml of a freshly prepared mixture of alcohol and  $\text{H}_2\text{SO}_4$  (6:1) and shake for a further 2 min. Extract the green colour with 5 ml of  $\text{CHCl}_3$  and determine its extinction (filter S72).

W. H. PARR

**3440. A colorimetric method for the estimation of glutamic acid in protein hydrolysates.** A. Zamir and N. Lichtenstein (*Anal. Chim. Acta*, 1955, **12** [6], 577-579).—The method depends on the conversion of glutamic acid to pyrrolidonecarboxylic acid (*cf.* Olcott, *Brit. Abstr. C*, 1944, 193) and the colorimetric determination of the latter by the method of Lipmann and Tuttle (*Brit. Abstr. C*, 1945, 276). *Procedure*.—Reflux 1.5 to 2 g of protein with 20 ml of aq. HCl (1 + 1) in a bath of stirred oil at 120° to 125° C for 35 hr. Add 1 g of purified bone charcoal and heat again for 1 hr. Cool, add 10 ml of water, filter, and wash the filter with 25 ml of water. Adjust the filtrate to between pH 3 and 4 by adding 7 N NaOH and autoclave for 4 hr. at 125° C. Filter if necessary and dilute to 100 ml.

To 4 ml add 4 ml of a 50 per cent. w/v soln. of hydroxylamine hydrochloride in 2 N NaOH, close the test-tube with a rubber stopper bearing a capillary vent, and heat for 15 min. in boiling water. Cool, and to 1.5 ml add 1.5 ml of water and 2.5 ml of a mixture of equal volumes of 2.5 N HCl, aq. trichloroacetic acid (15 per cent.) and a 5 per cent. soln. of ferric chloride in 0.1 N HCl. Determine the extinction with the Klett-Summer-son photo-electric colorimeter with filter 54. Calibrate the method with purified pyrrolidonecarboxylic acid and calculate on a 93.5 per cent. conversion of glutamic acid into pyrrolidonecarboxylic acid.

W. C. JOHNSON

**3441. The binding of histamine to plasma proteins.** O. Klammerth (*Biochem. Z.*, 1955, **327** [1], 62-71).—Histamine can be estimated spectrophotometrically by measurement of the extinction of the aqueous solution at 211.5 m $\mu$ . Beer's law applies over a range of 1 to 25  $\mu\text{g}$  per ml. The influence of pH, ions and proteins on the extinction curve is reported.

G. W. CAMBRIDGE

**3442. Estimation of histidine. I. Polarographic study and estimation of fluorodinitrobenzene.** P. E. Wenger, D. Monnier and S. Faraggi (*Anal. Chim. Acta*, 1955, **13** [1], 89-99).—1-Fluoro-2,4-dinitrobenzene (**I**) is proposed as a reagent for the polarographic determination of histidine. It has been examined polarographically at various pH values, and standardisations have been carried out at pH 5 and pH 10. The curve has two humps at the former pH but three at the latter unless the soln. has been allowed to stand for  $> 24$  hr. or has been warmed to a temp.  $> 60^\circ \text{C}$ . The determination at pH 10 is more accurate and permits **I** to be determined in amounts from 0.01 to 8 mg per 10 ml, with an error of  $\pm 7$  per cent. The selectivity is good, as the values of  $E_1^\circ$  for the first two humps are  $< 1 V$ . The total no. of electrons involved in the reduction is 9, and a possible reaction is suggested.

J. H. WATON

**3443. Modification of the procedure of Bates for the determination of tryptophan in proteins and its spectrophotometric determination.** J. C. Sanahuja (*An. Bromatologia*, 1955, **7** [1], 25-33).—The method of Bates (*J. Biol. Chem.*, 1937, **119**, vii) and its modification by Hess and Sullivan (*Ibid.*, 1944, **155**, 441) have been studied. With tryptophan alone, the colour formed with *p*-dimethylaminobenzaldehyde does not obey Beer's law. By using casein as the protective agent instead of gelatin, and allowing for the tryptophan in the casein, Beer's law is obeyed. Ten mg of casein (Difco) are used for weights of tryptophan from 0.03 to 0.3 mg.

L. G. L. UNSTEAD-JOSS

**3444. The estimation of 5-hydroxytryptamine (serotonin) in biological tissues.** S. Udenfriend, H. Weissbach and C. T. Clark (*J. Biol. Chem.*, 1955, **215** [1], 337-344).—The tissue is extracted with a borate buffer (pH 10; saturated with NaCl and *n*-butanol). The butanol extract is washed several times with the saturated buffer to remove impurities; addition of heptane and shaking with 0.5 M formate buffer at pH 4 then transfers the serotonin to the aq. phase, in which it is assayed. Three methods are described for the determination of serotonin. The first method involves spectrophotometric measurement at 275 m $\mu$ . The second involves a colorimetric estimation (at 540 m $\mu$ ) of the chromophore produced by reaction of serotonin with 1-nitroso-2-naphthol in the presence of nitrous acid. The colour is stable, and the sensitivity is

approx. the same as that of the u.v. method. It is the preferred method when tissue extracts contain large amounts of u.v.-absorbing material. The third method involves measurement of the fluorescence of serotonin in solution. A spectrofluorimeter is described which activates and measures emitted fluorescence continuously from 250 to 650  $\mu$ . Serotonin and other 5-hydroxyindoles have a max. activation at 295  $\mu$  and emit fluorescent light which has a max. at 330  $\mu$ . This method is extremely sensitive and will measure as little as 0.05  $\mu$ g of serotonin. J. N. ASHLEY

**3445. Electrophoresis of proteins in a column.** C. Dumazert, C. Ghiglione and M. Bozzi-Tichadou (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 123-126).—An illustrated description is given of an apparatus designed for the simultaneous electrophoretic migration of proteins through a column of powdered cellulose and their subsequent passage on to a strip of paper. The proteins travel slowly through the column forming separate rings, but more rapidly in the paper, where they are more widely separated and can be readily eluted by a capillary tube while the electrophoresis is proceeding. Curves showing the separation of serum albumin of human and bovine origin are provided, and reveal a much greater resolution than can be obtained by previous methods. P. HAAS

**3446. Application of zone electrophoresis to analysis of serum proteins. Technique of the horizontal-strip method and evaluation of its precision and accuracy.** C. A. J. von Frijtag Drabbe and J. G. Reinhold (*Anal. Chem.*, 1955, **27** [7], 1090-1095).—The precautions and technique required for quant. analysis of serum proteins by horizontal-strip paper-electrophoresis are described. The serum is applied to the strip by means of a paper applicator to avoid disturbance of the equilibrium established in the paper. After dyeing the strip with Amido black 10 B and making translucent, the absorbance is read with a densitometer. Good agreement is obtained with the Tiselius moving-boundary method, since the losses of albumin by "trailing" are almost compensated by greater dye-uptake. E. J. H. BIRCH

**3447. A new statistical method for the comparison of electrophoretic analyses of normal and pathological sera.** G. Herdan (*Klin. Wochschr.*, 1955, **33** [21-22], 538-539).—It is suggested that statistical evaluation of the results of electrophoretic analysis of serum proteins to distinguish between normal and pathological sera can be made by calculation of the mean time that a molecule of any given type will be observed in a small field of vision. H. F. W. KIRKPATRICK

**3448. Separation and characterisation of steroids from testicular tissue, vesicular-gland secretions and spermatozoa.** H. Breuer (*Biochem. Z.*, 1955, **327** [1], 6-19).—Methods of separation of free, conjugated and protein-bound steroids from tissues and secretions are described, together with details of chromatographic separation of fractions of these three groups on  $Al_2O_3$  columns. Identification of these fractions by paper chromatography in various solvents and by colour reactions with 3:5-dinitro-phthalic anhydride is also described. G. W. CAMBRIDGE

**3449. Urinary metabolites of administered cortisone. I. Steroids liberated by glucuronidase hydrolysis. [Assay of formaldehydogenic lipids.]** L. L. Engel,

P. Carter and L. L. Fielding (*J. Biol. Chem.*, 1955, **213** [1], 99-106).—Urine was treated with beef-liver  $\beta$ -glucuronidase to hydrolyse conjugates. After incubation for 3 days at 37° C, the hydrolysis mixture was extracted with dichloromethane. The residue from the extract was dissolved in ethanol; a suitable aliquot was transferred to the outer cell of a Conway unit and the solvent allowed to evaporate spontaneously; the residue was dissolved in 0.5 ml of triethyl phosphate. Two ml of 0.30 per cent. chromotropic acid in 15 M  $H_2SO_4$  were placed in the inner well and 1 ml of 0.02 M aq.  $NaIO_4$  in 0.15 M  $H_2SO_4$  was added to the outer well. After diffusion for 16 hr. at room temp. in the dark the contents of the inner well were heated over boiling water for 30 min., cooled and the absorbance measured at 570  $\mu$ . N. E.

**3450. A method for the estimation of urinary formaldehydogenic lipids which is free from formaldehyde retention.** L. L. Engel, P. Carter and L. L. Fielding (*J. Clin. Endocrinol.*, 1955, **15** [6], 765-767).—The method previously described by the authors (*Anal. Abstr.*, 1955, **2**, 3449) is shown to give a mean formaldehyde recovery of 99 per cent. when steroids are added to urine extracts. H. F. W. KIRKPATRICK

**3451. Micro-estimation on paper of catalytic activity. II. Application to the determination of enzyme activity.** S. Lissitzky and S. Bouchilloux (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 97-105).—The principle of the method for determining organic iodine (*Anal. Abstr.*, 1955, **2**, 3077) has been extended to enzymes, namely alkaline phosphatase, arginase and proteolytic enzymes. The method is approx. 100 times as sensitive as the classical methods, with an accuracy of  $\pm 5$  per cent.; it can be carried out on very small amounts of tissues. P. HAAS

**3452. Stable cholinesterase preparations as laboratory standards of activity.** J. H. Fleisher, S. Spear and E. J. Pope (*Anal. Chem.*, 1955, **27** [7], 1080-1083).—Purified cholinesterase from bovine red-blood cells is added to a stabilising medium (shown to lead to a high recovery of activity) of 0.3 M KCl, 0.5 per cent. bovine haemoglobin, 4 per cent. bovine albumin and 0.008 M phosphate buffer, at pH 7.4, to make a 1 per cent. soln. of enzyme for colorimetric, constant-pH, and electrometric methods of assay and a 0.2 per cent. soln. for the manometric method. Aliquots (0.02 ml from a micro-burette) are placed on Whatman No. 31 filter-paper and, after being dried, the standards are cut out and stored over desiccant in a refrigerator (activity falls to 99 per cent. in 6 months at 3° C and zero R.H.). A comparison is made of the different methods of determining the activity. The discs themselves show a variability of 2 to 3 per cent. E. J. H. BIRCH

**3453. Microdiffusion of acetic acid as an assay for acetylcholinesterase.** I. Serlin and G. C. Cotzias (*J. Biol. Chem.*, 1955, **215** [1], 263-268).—A simple direct assay of acetylcholinesterase activity is described. It involves direct titration after microdiffusion (in a Conway diffusion unit) of the acetic acid from the enzymic reaction mixture, which is kept at pH 3.0. Non-enzymic hydrolysis of the excess of labile substrate is prevented and diffusion of acetic acid is expedited by adding the sample to anhyd.  $Na_2SO_4$  at 4° C. By this method acetylcholinesterase made dilute enough to yield only 0.05  $\mu$ mole (3  $\mu$ g) of acetic acid per ml per hr.

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can be assayed. A unit of acetylcholinesterase activity is the amount per ml which catalyses the liberation of 0.1  $\mu$ mole of acetic acid per hr. at 37.5° C. J. N. ASHLEY

**3454. Chronometric method of determining polyphenol-oxidase activity. Potentiometric device for automatic determination of end-point.** L. L. Ingraham and B. Makower (*Anal. Chem.*, 1955, **27** [6], 916-918).—A potentiometric device is described for determining automatically the chronometric end-point in the estimation of polyphenol-oxidase activity. The time for aerobic oxidation of a known quantity of ascorbic acid is measured in the presence of the substrate catechol. A simple electrical circuit follows the e.m.f. change and automatically registers on a clock the time required to reach a p.d. selected as the end-point. An improved graphical method has been suggested for the calculation of the enzyme activity from the chronometric data at several concn. of ascorbic acid. O. M. WHITTON

**3455. A spectrophotometric method for the determination of creatine phosphokinase and myokinase.** I. T. Oliver (*Biochem. J.*, 1955, **61** [1], 116-122).—A rapid spectrophotometric method is described for the assay of creatine phosphokinase and myokinase in tissue extracts and homogenates. The method depends on the formation of adenosine triphosphate by these enzymes, which then reacts with glucose in the presence of  $Mg^{++}$  and hexokinase forming glucose-6-phosphate; this is oxidised by glucose-6-phosphate dehydrogenase with simultaneous reduction of triphosphopyridine nucleotide. Spectrophotometric determination at 340 m $\mu$  of the rate of this reduction gives the rate of formation of adenosine triphosphate, and hence the activity of the enzyme. The method is sensitive and an assay requires  $\approx 20$  min.; it permits the determination of activities in tissue preparations diluted to 1:20,000, which corresponds to  $\approx 300 \mu g$  of wet tissue. J. N. ASHLEY

See also Abstracts 3333, 3377, 3388, 3392.

### Drugs

**3456. The determination of the origin of opium. I. By means of the composition of the ash.** J. C. Bartlet and C. G. Farmilo (*Canad. J. Technol.*, 1955, **33** [3], 134-151).—A procedure has been developed, based on the composition of the ash, for determining the geographical origin of opium found in the illicit trade in narcotics. Methods are presented for determining K, Ca and Na by a flame photometer;  $PO_4^{'''}$  by a molybdenum blue procedure; and Si, Fe, Al, Ti, Mg, B, Mn, Mo, Cu, Sn and Pb spectrographically. The application of these methods to 102 opium samples of known origin is described. The median percentages of the constituents for Yugoslav, Turkish (druggist), Turkish (soft), Iranian, Indian and Far Eastern opium are given. The effects of accidental and deliberate contamination are taken into account by means of a correction factor. O. M. WHITTON

**3457. Quantitative elution of morphine from ion-exchange resins.** C. H. Van Etten (*Anal. Chem.*, 1955, **27** [6], 954-957).—A study is reported of the effects of degree of cross-linkage of the resin and of the pH and ionic strength of the eluting agent on the elution of morphine from strong cation and anion resins. Conditions were found that gave quantitative elution from resins of both types. A test on 10 consecutive samples of 10 mg of morphine

showed an average recovery of 10.05 mg with a standard deviation of  $\pm 0.22$ . The behaviour of other ampholytes and bases, e.g., lysine, codeine, narcotine and thiamine, has been examined under the same conditions of elution. O. M. WHITTON

**3458. The microchemical differentiation of morphine and nalorphine.** E. Pedley (*J. Pharm. Pharmacol.*, 1955, **7** [8], 527-532).—Many microcrystalline reagents give crystals with morphine (I) but not with nalorphine (II). Iodine-free HI gives crystals of different appearance with I and II, as also does picrolonic acid, but the distinction is less marked. Good separation of I and II may be obtained by chromatography on paper treated with 0.5 M KCl by development with a water-saturated mixture of *n*-butanol with HCl, acetic or citric acid;  $R_f$  values are given. X-ray diffraction data are given for bases and picrolonates of I and II.

A. R. ROGERS

**3459. A note on the polarographic determination of N-allylnormorphine [nalorphine].** J. Volke and V. Volkavá (*Českosl. Farmac.*, 1955, **4** [1], 20-21).—The method of Seagers *et al.* (*Brit. Abstr. C*, 1953, 172) was shown to be invalid as the polarography of nalorphine is only feasible in alkaline chloride soln. Moreover the height of the wave remains unchanged in concn.  $> 7 \times 10^{-4}$  M of the alkaloid and is strongly dependent on the pH of the soln. A polarographic method can be applied, however, to the nitroso derivative, when the height of the wave was found to be in linear relationship to the alkaloid concn. for solutions  $< 0.002$  M.

A. O. JAKUBOVIC

**3460. Compleximetric titration in pharmaceutical analysis. IX. Determination of codeine phosphate.** E. Adamová and J. Žýka (*Českosl. Farmac.*, 1955, **4** [1], 9-10).—After a review of the current methods and their shortcomings, a method for determining codeine phosphate, using  $MgSO_4$  soln., is described. Excess of standard  $MgSO_4$  soln. is added to the hot, slightly ammoniacal codeine soln., which (after filtering off the pptd.  $MgNH_4PO_4$ ) is back-titrated with EDTA (disodium salt) using Eriochrome black T as indicator [1 ml of 0.1 M EDTA (disodium salt)  $\equiv 0.0137$  g of  $NaNH_4HPO_4$ ]. The titration is carried out in  $NH_4Cl$ -aq.  $NH_3$  buffer. The method is accurate to  $\pm 1$  per cent. with 10 to 20 mg of the codeine phosphate, and is suitable for semi-micro determination of the substance in tablets, etc.

A. O. JAKUBOVIC

**3461. Chromatography of organic acids in cured tobacco.** F. E. Resnik, L. A. Lee and W. A. Powell (*Anal. Chem.*, 1955, **27** [6], 928-931).—One sample is used for the determination of total organic acidity, the qual. identification of some polybasic organic acids by paper chromatography and the quant. determination of these individual acids by column partition chromatography. The acids are purified by passing a filtered extract of the tobacco at pH 8 through an anion-exchange column (Dowex 1) and washing out with 1.5 N ammonium carbonate. After decomposing the ammonium carbonate by boiling, the soln. is passed through a cation-exchange column (Amberlite IR-112) and the eluate is titrated with 0.02 N NaOH. The solvent for the paper chromatography is prepared by refluxing a mixture of *n*-pentanol, water and formic acid (20:12:1) for 1 hr., drawing off the water and adding 0.05 per cent. of 8-hydroxyquinoline. Other solvents used are phenol, water and formic acid (75:24:1) containing 0.05 per cent.

of 8-hydroxyquinoline; mesityl oxide, water and formic acid (7:10:1) (shaking and separating the organic layer); and benzyl alcohol, *tert*-butanol, isopropanol, water and formic acid (30:10:10:10:3). For quant. determination of the acids a silica-gel column is used. The dry ammonium salts are dissolved in 1 ml of  $N H_2SO_4$  then mixed with 1 g of purified silica, suspended in water-saturated  $CHCl_3$  and poured on to the column. The individual acids are eluted with *tert*-butanol-chloroform in the following proportions: fumaric acid (8:92), succinic acid (13:87), oxalic acid (20:80), malic acid (25:75) and citric acid (30:70). O. M. WHITTON

**3462. The quantitative estimation of digitalis glycosides by means of Keller-Kiliani and Pesze-Dequeker reagents.** R. Dequeker and N. Loobuyck (*J. Pharm. Pharmacol.*, 1955, 7 [8], 522-526).—The Pesze-Dequeker reagent (I) and the Keller-Kiliani reagent of Rowson (II) have been used to estimate deacetyldigilans and B, digitoxin and gitoxin as individual glycosides or in mixtures. I and II are equally accurate, but I is more convenient and ten times as sensitive as II. The presence of digitoxigenin, gitoxigenin or digitalinum verum does not influence the results. A. R. ROGERS

**3463. Polarographic measurement of L-nor-adrenaline and L-adrenaline.** J. Henderson and A. S. Freedberg (*Anal. Chem.*, 1955, 27 [7], 1064-1066).—Stock solutions ( $10^{-2}$  to  $10^{-3} M$ ) of adrenaline or its acid tartrate in 2 per cent. acetic acid are prepared, and an aliquot of  $\approx 10^{-3}$  millimole is made up to 5 ml with 2 per cent. acetic acid. Six millimoles of  $0.1 N KIO_3$  per millimole of adrenaline are added and the solution is stirred for 4 min.;  $2 N H_2SO_4$  (1 ml) is then added and the colour change indicates substitution of the I on the adrenochrome indole ring; 1.7 millimoles of KI per millimole of adrenaline are then immediately added. Aliquots of this solution are put into a polarographic cell with 1 ml of 0.5 per cent. gelatin and made up to 5 ml with 0.1 M acetic acid-acetate buffer. Oxygen is removed with purified nitrogen and the solution is polarographed with the dropping-mercury electrode. Noradrenaline is treated similarly but solutions are more stable in Na acetate solution. The  $E_1$  for iodo-adrenochrome is +0.03 V and, for iodonoradrenochrome, +0.02 V vs. the S.C.E. under these conditions. There is a linear relationship for concn. - diffusion current for aliquots containing 1 to 50  $\mu g$ . The method is checked titrimetrically and the error estimated as 5 to 10 per cent. The applicability of the method to biological solutions and the possibility of separation of adrenaline and noradrenaline by chromatography before polarography are discussed.

E. J. H. BIRCH

**3464. Paper chromatography of nicotine and related compounds.** L. Leiserson and T. B. Walker (*Anal. Chem.*, 1955, 27 [7], 1129-1130).—A standardised procedure for paper chromatography of tobacco extracts and smoke is described, in which the paper is first sprayed with an acetate buffer (pH 5.6) and air-dried. The extract (10 to 50  $\mu g$ ) is applied to the starting point and the sheet is allowed to equilibrate with water vapour. The chromatogram is developed for 16 hr. at 74° F with butanol saturated with acetate buffer, pH 5.6. The spots of tobacco alkaloids are revealed by *p*-aminobenzoic acid after exposure to BrCN. The effect of the buffer on the chromatogram is discussed and it is pointed out that spraying with NaCl solution is advantageous.

E. J. H. BIRCH

**3465. Evaluation of [plant] materials containing mucilaginous matter.** R. Hegnauer (*Pharm. Weekbl.*, 1955, 90 [16], 545-548).—This review covers descriptions of the available analytical methods and tabulated results and standards for 21 different mucilaginous drugs, including seeds of 11 species of *Plantago*. P. S. ARUP

**3466. A spectrophotometric assay for aureomycin [chlortetracycline] hydrochloride.** L. J. Ravin and A. E. James (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, 44 [4], 215-216).—A method of assay for chlortetracycline hydrochloride (I) in tablets, capsules and other pharmaceutical products is described. Procedure—An aliquot of the sample containing  $\approx 25$  mg of I is dissolved in 150 ml of water and 20 ml of 2 per cent. conc. molybdophosphoric acid are added. The pH is adjusted to between 5.5 and 6.5 by the dropwise addition of 10 per cent. NaOH soln. and the vol. is made up to 1 litre. The absorbance of the coloured solution is measured at 405  $\mu\mu$  and the concn. of I is determined by comparison with a standard. Results agree well with those obtained by the fluorimetric method (Levine *et al.*, *Brit. Abstr. C*, 1950, 18).

N. M. WALLER

**3467. Interference of sucrose in the plate assay of polymyxin B.** N. Knowlton, E. Broomfield and J. Hernan (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, 44 [4], 231-234).—A statistical study of the interference of sucrose in the polymyxin-B plate assay is described and 95 per cent. of the existing variation is explained. The procedure presents a means of correcting for this interference so that dilutions of the antibiotic containing differing sucrose concn. may be determined by the use of only one reference dilution. A nomogram is presented from which the corrected results may be read.

N. M. WALLER

**3468. A potentiometric non-aqueous assay for barbiturates and their preparations.** C. J. Swartz and N. E. Foss (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, 44 [4], 217-218).—From a quant. study on a series of barbiturates (those proposed for admission in U.S.P. XV), a non-aqueous potentiometric assay method is established, that is suitable for routine analyses on the drugs and their pharmaceutical preparations. A 0.1 to 0.2-g sample of the powdered, dried barbiturate is dissolved in 5 ml of polyethylene glycol 400 and 45 ml of chloroform and the solution is titrated with 0.1 N sodium methoxide in a Fisher titrimeter. The metal salts of the barbiturates are first dissolved in water and, after acidification, extraction with chloroform is effected.

N. M. WALLER

**3469. The polarographic determination of acriflavine.** A. J. Zimmer and K. Mansur (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, 44 [4], 204-206).—The polarographic behaviour of acriflavine (I) in acid and basic solutions is investigated and, since it behaves as a single substance, a polarographic method for its determination is described. Solutions of approx. 0.25 per cent. of I in 0.1 M HCl are polarographed. Equations are given to determine the half-wave potential in solutions of varying pH and concn. The method is applied to the quant. determination of I in powder, tablets and ointment.

N. M. WALLER

**3470. Colorimetric determination of *m*-aminophenol in 4-aminosalicylic acid with 4-aminophenazone.** J. Franc (*Českosl. Farmac.*, 1955, 4 [1], 4-6).—4-Aminophenazone (I) in alkaline solution

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**3471. Id. amines.** V. Amer. Pharm. 316).—Qua crystalline sympathom amphetamine methylhex propylmeth amphetamine prepared benzenesul benzoates. tion of 2: toluene by also descri

**3472. Po. B. Novotr 662-663).— tion of no where it i 0.5 mg per and nitrat polarograph Evaporate to dryness. Add 1 ml the bath dryness. HNO<sub>3</sub> (65 Add 10 ml up to 14.5 carried out sensitive to I in an u treated as a known a**

**3473. A mercurial (J. Amer. Mercurial mercuric group (e.g. H<sub>2</sub>SO<sub>4</sub> react be titrate Procedure-taining  $\approx$  Add conc. and keep i FeNH<sub>4</sub>(SC with 0.1)**



and in the presence of an oxidising agent gives a red coloration with *m*-aminophenol (II) which obeys the Beer - Lambert law in the concn. range used (0 to 0.2 mg in 50 ml). 4-Aminosalicylic acid (III) gives a similar coloration in weakly alkaline solutions, but this is suppressed by carrying out the reaction in 25 per cent. aq.  $\text{NH}_3$  soln. Potassium ferricyanide was used as the oxidising agent, and the dependence of the extinction coefficient upon its concn. is shown by a graph. The solution for the colorimetric determination was prepared by taking 10 ml of a 0.4 per cent. aq. soln. of the III under examination, 10 ml of  $\text{H}_2\text{O}$ , 2 ml of 3 per cent. aq. I soln. and 6 ml of 2 per cent.  $\text{K}_3\text{Fe}(\text{CN})_6$  soln. and making up to 100 ml with 25 per cent. aq.  $\text{NH}_3$  soln. The results for concn. of II up to 0.5 per cent. accord to within  $\approx 10$  per cent. with those obtained by extraction methods.

A. O. JAKUBOVIC

**3471. Identification of some sympathomimetic amines.** W. H. A. Fischer and E. M. Plein (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [5], 313-316).—Qualitative tests utilising the m.p. of crystalline derivatives of ten commonly used sympathomimetic amines (amphetamine, dexamphetamine, ephedrine, methoxyphenamine, 1-methylhexylamine, phenylpropanolamine, phenylpropylmethylamine, racephedrine and hydroxyamphetamine) are described. The derivatives prepared are the phenylthioureas, benzamides, benzenesulphonamides and 3:5- and 2:4-dinitrobenzoates. An improved method for the preparation of 2:4-dinitrobenzoic acid from 2:4-dinitrotoluene by oxidation with  $\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  is also described.

G. R. WHALLEY

**3472. Polarographic determination of neostigmine.** B. Novotný (*Chem. Tech., Berlin*, 1954, **6** [12], 662-663).—The method was devised for the estimation of neostigmine (I) in medical preparations, where it is usually present in a concentration of 0.5 mg per ml. It is based on the hydrolysis of I and nitration of the resulting phenol, followed by polarography of the nitro derivative. *Procedure*.—Evaporate 0.2 to 0.6 ml of a 0.1 per cent. soln. of I to dryness in a 50-ml beaker on a water bath. Add 1 ml of KOH soln. (20 per cent.), warm on the bath for 20 min., then again evaporate to dryness. Add 0.5 ml of water and 2 ml of conc.  $\text{HNO}_3$  (65 per cent.), warm for 20 min., and cool. Add 10 ml of KOH soln. (20 per cent.) and make up to 14.5 ml with water. The estimation is then carried out by polarography, with a galvanometer sensitive to  $10^{-8}$  amp. To determine the concn. of I in an unknown, solutions of the unknown are treated as described above, both with and without a known amount of I.

K. J. GARDNER

**3473. A note on a simple assay method for certain mercurial diuretics.** E. E. Theimer and P. Arnow (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [6], 381).—Mercurial diuretics, formed by the addition of alkyl mercuric salts to compounds containing an allyl group (e.g., mersalyl), when dissolved in 50 per cent.  $\text{H}_2\text{SO}_4$  react quantitatively with KSCN and may be titrated as inorganic mercuric compounds. *Procedure*.—Mix with water (10 ml) a sample containing  $\approx 200$  mg of Hg and chill in an ice-bath. Add conc.  $\text{H}_2\text{SO}_4$  (10 ml), dropwise, with agitation and keep in the ice-bath for a further 10 min. Add  $\text{FeNH}_4(\text{SO}_4)_2$  soln. (8 per cent.) (2 ml) and titrate with 0.1 N KSCN. Halide ions interfere and a

preliminary test for their absence should be made.

H. B. HEATH

**3474. An improved assay for magnesium citrate solution.** D. D. Abbott and L. A. Reber (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, **44** [5], 287-289).—Volumetric methods for the determination of Mg and the total citric acid content of Mg citrate are described, the results of which are comparable with those of the official U.S.P. methods. *Magnesium*.—Magnesium citrate soln. (10 ml containing about 25 mg) is freed from  $\text{CO}_2$  and diluted to 100 ml, a 25-ml aliquot is added to 50 ml of EDTA (disodium salt) soln. (1 per cent. w/v, previously standardised against a soln. of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and then set aside for 10 min. A buffer soln. (67.5 g of  $\text{NH}_4\text{Cl}$  and 570 ml of conc. aq.  $\text{NH}_3$  per litre) (20 ml) is added with 2 drops of "Inhibited Versenate Indicator" and the excess of the EDTA (disodium salt) soln. is back-titrated with a standard  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  soln. *Total citric acid*.—A 25-ml aliquot of the citrate soln. (concn. as above) is heated almost to boiling point, and the hot soln. is poured through a column (300 mm  $\times$  8 mm) of Amberlite IR-120 (H) resin; the eluate and washings are cooled and titrated with 0.1 N NaOH to phenolphthalein. The ion-exchange method is not specific for citric acid since all the cations present are replaced by  $\text{H}^+$  and are titrated by the alkali.

G. R. WHALLEY

See also Abstracts 3411, 3480, 3481, 3501, 3502, 3503, 3504, 3519.

#### Food

**3475. The identification of water-soluble organic acids in food by paper chromatography.** E. Becker (*Z. Lebensmittelforsch.*, 1954, **98** [4], 249-257).—It is shown that the  $R_f$  values of the non-volatile and phosphoric acids depend on their concn., and on their presence in the free form or as various salts. The formation of insoluble salts is another source of error. Extraction with  $\text{H}_2\text{O}$  should be followed by extraction with 2 per cent.  $\text{H}_2\text{SO}_4$ . The volatile acids are separated by distillation. The non-volatile acids, in a free form, are subjected to chromatography as a 2 to 4 per cent. soln., with *n*-butanol - benzyl alcohol - 85 per cent. formic acid - water (7:7:1:2) as solvent. The chromatogram is developed successively with bromocresol green to detect adipic, lactic and citric acids; with ammonium vanadate to detect tartaric acid; and with perchloric acid - ammonium molybdate for phosphoric acid. The volatile acids are chromatographed in duplicate as their ammonium salts, with a solvent of *n*-butanol - 1.5 N aq.  $\text{NH}_3$  (5:1). One chromatogram is developed with chlorophenol red to detect acetic and propionic acids; the other with aq.  $\text{NH}_3$  and  $\text{AgNO}_3$  to detect formic acid.

W. H. PARK

**3476. Determination of tannins and related polyphenols in foods. Comparison of Loewenthal and Pro methods.** C. J. B. Smit, M. A. Joslyn and A. Luktan (*Anal. Chem.*, 1955, **27** [7], 1159-1162).—The Loewenthal (permanganate titration) and the Pro (colorimetric with Folin - Denis reagent) methods are compared for pure phenolic substances, for commercial tannins and for fruit tannins from various green and ripe fruit. The changes in redox potential during the Loewenthal titrations were recorded and are shown not to be useful for observing the progress of the titration. With the response of tannic acid U.S.P. to the two methods as standard,

the Loewenthal method gives very low results with resorcinol and very high with quinol. The commercial tannins give higher results by the Pro method. The fruit tannins give better agreement possibly because a mixture of substances is determined. The change in the absorption spectrum during the titration when the max. at 610 m $\mu$  disappears and the min. at 400 m $\mu$  becomes a max. suggests the possibility of following the titration colorimetrically.  
E. J. H. BIRCH

**3477. The "filth" test.** E. Hanssen (*Z. LebensmittUntersuch.*, 1954, **98** [6], 405-411).—The application of the test used in the U.S.A. (involving defatting, decomposition with acid, extraction with liquid paraffin and microscopic examination) for adulteration of foodstuffs by animal and plant material is discussed, with particular reference to flour and sugar. Nineteen photomicrographs show the appearance of rodent hairs, and of the mouth-parts, legs, wing scales, tracheae, etc., of insects.  
A. R. ROGERS

**3478. An electrophotometric semi-micro method for the quantitative determination of diastase in honey.** H. Gontarski (*Z. LebensmittUntersuch.*, 1954, **98** [3], 205-213).—The diastatic activity of honey is determined by assaying the residual starch in a substrate of known starch content after mixing known amounts of substrate and honey and setting aside for 15 and 30 min. in a thermostat at 35° C. The pH is important, and is generally optimal between pH 4.7 and 5.2, but varies for different honeys. Determinations should always be made at three different pH values (4.2, 4.8 and 5.4 were arbitrarily chosen) and the highest diastatic value is taken as the correct result. The residual starch is assayed by adding a solution of iodine, determining the absorption of the resulting blue colour and calculating the starch concentration from a calibration curve. A fresh curve must be prepared for each batch of starch solution, but if the solution is sterile its age has no influence. Accurate temperature control throughout is important.

P. S. STROSS

**3479. Application of the Kolthoff-Kruisheer method to the analysis of sugar mixtures.** S. Gianferrara and E. Pascucci (*Chim. e Ind.*, 1955, **37** [7], 545-547).—The Kolthoff-Kruisheer method is used to determine a mixture of sugars such as occurs in hard candies containing sucrose, commercial glucose syrup, lactose and invert sugar formed during manufacture. The methods used are (a) determination of dry residue by sp. gr. and refractive index, (b) polarimetry before and after inversion, (c) oxidation of aldose with iodine in alkaline solution, acidification, removal of excess of iodine with sodium sulphite, neutralisation, and determination of fructose with Fehling's solution.  
C. A. FINCH

**3480. The examination of commercial sorbitols with special reference to their suitability for diabetic diets.** A. J. Kennedy-Ripon and R. E. A. Mapes (*Analyst*, 1955, **80**, 568-569).—An examination of commercially available sorbitol syrups revealed the presence of saccharide impurities, e.g., maltose and glucose, due to incomplete hydrolysis and reduction of the starch hydrolyses used in the manufacture. Application of the modification by Sichert *et al.* (*Brit. Abstr. B*, 1937, 275) of the Bertrand method, whereby the amount of available reducing sugars is determined, showed that commercially available sorbitol syrups vary widely in their content of sugars.  
A. O. JONES

**3481. Solanine, glycoside of the potato. III. An improved method of extraction and determination.** L. C. Baker, L. H. Lampitt and O. B. Meredith (*J. Sci. Food Agric.*, 1955, **6** [4], 197-202).—The method of Rooke *et al.* (*Brit. Abstr. BIII*, 1943, 81) for the determination of solanine in potato has been modified. The new method is more rapid, requires less alcohol and gives consistently higher results than the old. It is applicable to cooked potato, and to reconstituted freeze-dried potato. *Procedure*—Comminute the tubers (20 g) in a top-drive macerator with 95 per cent. alcohol (150 ml), add glacial acetic acid (3 ml) and extract for 16 hr. in a Soxhlet apparatus. Evaporate to 1 or 2 ml and wash through a No. 4 filter-paper into a centrifuge tube with 5 per cent. H<sub>2</sub>SO<sub>4</sub> (10 ml). Adjust the pH to 9.4 by adding conc. aq. NH<sub>3</sub>. Heat to 80° C to flocculate the ppt., and keep overnight at 4° C. Centrifuge, wash the ppt. with 1 per cent. aq. NH<sub>3</sub> (10 ml) and dissolve in 1 per cent. H<sub>2</sub>SO<sub>4</sub> (10 ml). To this soln. (2.5 ml) add conc. H<sub>2</sub>SO<sub>4</sub> (5 ml), dropwise, during 3 min., shaking vigorously; after 1 min. add 1 per cent. formaldehyde soln. (2.5 ml), dropwise, during 2 min. Measure the colour density after 90 min. The absorption max. is at 570 m $\mu$  with a mol. extinction coeff. of 10,110. For routine purposes, an Ilford 605 filter may be used, when  $\epsilon$  = 8448; the absorption-concn. graph is virtually linear over the range 125 to 1250  $\mu$ g of solanine per 10 ml of coloured soln.

A. R. ROGERS

**3482. Reasons for discoloration of steamed potatoes. I. The effect of phenolic substances.** F. Kiermeier and E. Rickerl (*Z. LebensmittUntersuch.*, 1955, **100** [6], 441-449).—The presence of chlorogenic acid (and, to a lesser degree, of caffeic acid) was found to be one of the reasons for the discoloration of steamed potatoes. It was possible to determine the content of chlorogenic acid (up to 37 mg per 100 g) and to identify the presence of caffeic acid and quinic acid in alcoholic extracts of raw and steamed potatoes, peels and shoots by means of paper-chromatographic analyses, colour reactions, *R<sub>F</sub>* values and solubility tests. Concentrates (0.01 to 0.03 ml) of pH 5.5 containing the isolated phenolic substances (techniques of isolating with Pb acetate and preparing extracts of known concentration are described in detail) were placed on Whatman No. 1 paper and chromatographed (ascending method), with butanol-acetic acid-water (4:1:5) as solvent. The strips were developed with 2 per cent. molybdophosphoric acid solution and subsequent exposure to ammonia vapour. The extinction of the dried bluish-grey spots was measured by a photometer. Their area was determined and the contents of chlorogenic acid were calculated with the aid of a calibrated control curve, similarly prepared with known amounts of substance.  
S. C. I. ABSTR.

**3483. Improvements in a method for determination of the colour of milk and milk products.** F. H. Tinkler, R. C. Stribley and F. W. Bernhart (*J. Dairy Sci.*, 1955, **38** [6], 634-639).—In a modification of the method of Choi *et al.* (*Brit. Abstr. C*, 1950, 69) 0.01 per cent. aq. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is recommended in place of I in 10 per cent. KI as colour standard. Greater sensitivity is obtained by decreasing the wavelength at which measurements are made, and the test is made more general by calculating the colour on the basis of the average protein content of milk. Results obtained on various colorimeters and a spectrophotometer are compared and the

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W. H. C. SHAW

**3484. The demonstration of diacetyl, acetoin and butane-2,3-diol during incipient decomposition of meat, by means of the micro-beaker method.** W. Kromrey and C. Griebel (*Z. LebensmittUntersuch.*, 1954, **99** [3], 196-210).—The micro-beaker method is briefly described. With this method the formation of diacetyl (I) in decomposing meat was demonstrated with the following reagents: nickel dimethylglyoxime (sensitive to 0.001  $\mu$ g per 0.1 ml), benzhydrazide (10  $\mu$ g per 0.1 ml) and *p*-nitrophenylhydrazine. Photomicrographs are given of the crystals formed with these compounds. It was found that formation of I is most pronounced at pH 6.5 to 6.9, decreases with increasing temperature and increasing R.H., and may be prevented completely by u.v. light; I is not formed in the absence of O or of bacteria. Butane-2:3-diol and acetoin, which are intermediates in the formation of I, were also demonstrated by the micro-beaker method.

K. J. GARDNER

**3485. The analysis and evaluation of pectins.** K. Tüfel and G. Feldmann (*Chem. Tech., Berlin*, 1954, **6** [10], 525).—A brief review is given of the structure, mechanism of gel formation and analysis of pectins. (22 references.)

K. J. GARDNER

**3486. Photometric determination of caffeine in tea-infusions.** J. Richter (*Z. LebensmittUntersuch.*, 1954, **99** [4], 267-269).—A new colorimetric method is described for the determination of caffeine in tea-infusions. The results are not affected by the presence of sugar, milk, cream, lemon juice or brandy. *Procedure*.—Shake the sample (10 ml) for 1 min. with  $\text{CHCl}_3$  (20 ml) and 15 per cent. aq. NaOH soln. (0.5 ml). To 10 ml of the organic layer add  $\text{H}_2\text{O}$  (5 ml), and remove the  $\text{CHCl}_3$  by evaporation. Cool, and transfer to a Jena G4 filter which already contains 16 per cent.  $\text{H}_2\text{SO}_4$  (2 ml) and 0.1 N I (2 ml). After a minute, filter by applying suction. Dissolve the ppt. by drawing methanol (25 ml) and  $\text{H}_2\text{O}$  (25 ml) through the filter, and compare the absorption of the yellow solution with a reagent blank, a Pulfrich photometer (filter S47 and 2-cm cell) and a standard curve being used.

A. R. ROGERS

**3487. Stimulating drinks containing caffeine. II. The determination of caffeine and phosphoric acid.** V. Hamann (*Z. LebensmittUntersuch.*, 1954, **98** [3], 213-218).—The procedure described avoids the emulsions that are normally formed when caffeine is extracted from lemon drinks with chloroform. To 40 ml of the degassed drink add  $\text{CuSO}_4$  solution (20 per cent.) (4 ml) and N NaOH (4 ml) and make up to 60 ml. Shake well, filter and transfer a portion (40 ml) of the filtrate to a separating funnel containing chloroform (5 ml). Add 5 per cent.  $\text{KMnO}_4$  solution dropwise (about 1 ml) to a permanent pink colour, followed by freshly prepared  $\text{FeSO}_4$  soln. (10 per cent.) (3 ml) and  $\text{H}_2\text{SO}_4$  (sp. gr. 1.35) (0.3 to 0.5 ml). Set aside for 15 min. and extract the now pale-blue or yellow-green solution with chloroform (4  $\times$  15 ml, and 1  $\times$  10 ml). Transfer the chloroform layers to a Kjeldahl flask, boil off the chloroform and determine the nitrogen in the usual manner. Phosphoric acid is estimated by igniting the evaporated drink with magnesium acetate, followed by gravimetric or volumetric estimation of the phosphate, or preferably by the following method. To the sample (15 ml) add

$\text{KMnO}_4$  solution (5 per cent.) (1 ml), set aside for 10 min. and add conc.  $\text{HNO}_3$  (2 ml). Shake until the solution becomes clear and add aq.  $\text{NH}_3$  ( $\approx$  10 per cent.) ( $\approx$  6 ml) until the solution becomes just turbid; just clear the solution again with 2 N  $\text{HNO}_3$ , dilute to 60 ml and filter. To the filtrate (40 ml) add water (10 ml),  $\text{HNO}_3$  (sp. gr. 1.4) (10 ml),  $\text{NH}_4\text{NO}_3$  soln. (34 per cent.) (20 ml) and heat to boiling point. Precipitate the phosphate by adding ammonium molybdate solution (3 per cent.) (10 ml), filter, dry and weigh the ppt.

P. S. STROSS

**3488. Further contributions on the prediction of malt extracts from the results of barley analyses with Bavarian barleys of the 1953 and 1954 crops.** R. Heuss (*Brauwissenschaft*, 1955, **8** [4], 68-72).—Investigations using mathematical formulae for the prediction of malt extracts have been carried out with Bavarian barleys of the 1953 and 1954 crops. These formulae are based on the protein content and thousand-corn weights of the barley. Eleven formulae were investigated and the following formula,

$$\text{extract} = 83.9 - 0.75 E + 0.10 K,$$

where  $E$  = protein (per cent.) and  $K$  = 1000-corn wt., when used for the 1954 Bavarian barley crop, produced results close to the actual malt extracts obtained (*cf. Anal. Abstr.*, 1955, **2**, 1342).

G. H. BAKER

**3489. Possibilities and limitations of rapid moisture determination [in brewing materials].** K. Fuss (*Brauwelt*, 1955, **B** [35-37], 489-492; 510-513).—Methods based on the use of i.r. irradiation, alternating current, electrical or vapour-pressure measurements, or chemical reactions are unsuitable. Two drying ovens on the (German) market equipped with forced ventilation are suitable for rapid routine work (*cf. Brit. Abstr. C*, 1953, 480). P. S. ARUP

**3490. Evaluation of quaternary ammonium compounds as disinfectants in the brewing industry.** B. Jacobsson (*Brauwelt*, 1955, **B** [41-42], 647-652).—The efficiency of the disinfectants is compared with that of chloramine T by spraying separate areas of the corroded and infected surface of a brewing vessel, first with a soln. of the disinfectant and then with melted wort gelatin. A funnel-shaped hood is used to localise the spraying and to avoid air-infection. Each separately treated area is covered with a sterile Petri dish, and observed for the growth of colonies. A laboratory method is described in which the centrifuged sediment from 50 ml of a suspension containing a known no. of cells of a test organism (*Saccharomyces carlsbergensis*) is treated, during 10 min., with the disinfectant solution; the sediment is then centrifuged off, washed and tested for living cells by plating on wort gelatin. Data are given for several quaternary ammonium compounds and phenol used at different concn., temp. and pH against various yeasts and lactic acid bacteria. The temp. coeff. for cetylpyridinium chloride varies very considerably with the concn.

P. S. ARUP

**3491. Determination of carbon dioxide in beer.** J. Blom (*Brauwelt*, 1955, **B** [41-42], 645-646).—The beer (250 ml, or the contents of a bottle) is carefully mixed with 10 ml of 50 per cent. carbonate-free NaOH soln., under conditions precluding the absorption of atmospheric  $\text{CO}_2$ , and 10 ml of the mixture are measured into one of two 50-ml flasks which are connected in series with one another and with an air-circulating pump; the second flask

contains 25 ml of 0.1 N Ba(OH)<sub>2</sub> for the quant. absorption of the CO<sub>2</sub> liberated from the alkaline beer in the first flask on acidification with 5 ml of N HCl, added through a dropping-funnel. After running the pump for 8 to 10 min., the CO<sub>2</sub> in the sample can be determined correctly to two significant figures, by back-titration of the 0.1 N Ba(OH)<sub>2</sub>, the calculation being based on the average contents of the beer- or -sampling bottle, and the average sp. gr. of the beer, or alternatively on the wt. of the beer.

P. S. ARUP

**3492. Paper-chromatographic identification of non-volatile acids, formed during fermentation of grape-must.** P. Böhlinger and J. Wenzler (*Z. LebensmittUntersuch.*, 1955, **100** [6], 458-462).—The presence of small amounts of lactic acid, formed during fermentation of grape-must, was confirmed by paper chromatography, after complete elimination of butane-2:3-diol (an interfering by-product of fermentation) through steam-distillation. Experiments were carried out with numerous samples of must (4 to 100  $\mu$ l) at different stages of fermentation. Filtered wine (from must free from lactic acid) was chromatographed on paper strips by the descending method, with butanol - benzyl alcohol - 85 per cent. formic acid - water (7:7:1:2) as solvent and bromocresol green as developer. Apart from spots of lactic acid and known non-volatile acids (citric, tartaric, succinic, etc.), the chromatogram showed other, not yet identified, spots, which probably include those of glutaric and quinic acid.

S.C.I. ABSTR.

**3493. Colorimetric determination of malic acid in wines and fruit juices.** E. Kiehlhöfer, H. Aumann and M. Specht (*Z. LebensmittUntersuch.*, 1955, **100** [6], 449-458).—It was found that Nitschke's technique of determining malic acid by a colour reaction with 1-naphthol in conc. H<sub>2</sub>SO<sub>4</sub> gave unsatisfactory results, especially with sugar-containing wines and juices, owing to its positive reaction with ingredients other than malic acid. The effect of these interfering substances was examined and eliminated by suitable pre-treatment of the material. A sample of clear wine (100 ml) was filtered through a prepared anion-exchange resin (Permutit E3 in OH form), washed with 500 to 1000 ml of H<sub>2</sub>O (according to the sugar content) and eluted with 100 ml of N KOH. The last 90 ml of the alkaline eluate were collected, brought to pH 3.4 to 3.5 with 6 N HCl and used for the determination of malic acid (as Ba malate) with 1-naphthol in conc. H<sub>2</sub>SO<sub>4</sub> (0.5 g in 10 ml). Results (tabulated) show a relative error of < 4 per cent.

S.C.I. ABSTR.

**3494. The quantitative determination of benzaldehyde and vanillin in foodstuffs.** H. Böhme and O. Winkler (*Z. LebensmittUntersuch.*, 1954, **99** [1], 22-27).—If a sufficient quantity of vanillin or benzaldehyde is present in the food being examined, the volumetric method of Maltby and Primavesi (*Brit. Abstr. C*, 1950, 56) is recommended. The oxime is formed by using hydroxylamine hydrochloride solution, and the liberated HCl is titrated. The gravimetric estimation in which 2:4-dinitrophenylhydrazine is used is also suitable. If only small quantities are available a colorimetric method, based on the formation of the 2:4-dinitrophenylhydrazone and measurement of the extinction in methanolic KOH solution, is recommended. The determination of vanillin in vanilla sugar, and benzaldehyde in almonds and marzipan, is described.

P. S. STROSS

**3495. Extraction of colouring agents for foodstuffs with quinoline and their identification by chromatography on aluminium oxide "plates."** M. Mottier and M. Poterat (*Anal. Chim. Acta*, 1955, **13** [1], 46-56).—A rapid scheme for separating and identifying artificial colouring matter from foodstuffs is described. Water-soluble dyes are extracted with quinoline from an aq. soln. or suspension of the sample buffered at pH 3. Fat-soluble dyes are adsorbed directly on to the activated Al<sub>2</sub>O<sub>3</sub> from a soln. of the sample in a solvent of weak eluting power. The dyes are then separated chromatographically on "plates" of Al<sub>2</sub>O<sub>3</sub>, and the results are compared with known dyes submitted to the same techniques. If required, the chromatograms are preserved by percolating with molten paraffin wax or cetyl alcohol and allowing to solidify.

J. H. WATON

**3496. Limitations of the periodic acid method for the determination of monoglycerides in oils.** C. S. Martin Pérez and M. T. Santos Molero (*Grasas y Aceites*, 1955, **6** [3], 135-140).—Apparent monoglyceride contents of fish-liver oils, determined by the periodic acid method, are higher than is consistent with the hydroxyl value of the oil, even assuming the whole of this hydroxyl to be present as monoglyceride. The unsaponifiable constituents of the oil, e.g., vitamins A and E, react with periodic acid, but are not present in sufficient concn. to explain the results. The fatty acids obtained from the oil give apparent monoglyceride contents similar to those of the oils and the values remain unchanged on acetylation. Peroxidation of the oils by blowing with air has only a minor influence on the result. Fractional distillation under vacuum of the ethyl esters of the fatty acids effected some concn. of the material reactive to periodic acid, but no sharp separation. The anomalous results appear to arise from reaction between the reagent and the oil double-bonds.

L. A. O'NEILL

**3497. The detection of horse fat in beef and pork fat (suet and lard).** C. R. Franzke (*Z. LebensmittUntersuch.*, 1954, **99** [1], 27-33).—It is found that the content of linoleic (I) and linolenic (II) acids of horse fat is very much higher than that of beef or pork fat. The admixture of horse fat in the other fats can be detected by determining the sum of I and II in the sample of fat. This is more sensitive than determining II alone, and is best done by precipitating and weighing the light-petroleum-insoluble polybromostearic acid. *Procedure*—Saponify 1 to 2 g of the fat and extract the unsaponifiable material. Acidify the aqueous soap solution with N HCl (20 ml), add saturated NaCl solution (50 ml), followed by light petroleum (20 ml), shake, separate the light-petroleum layer, dry with Na<sub>2</sub>SO<sub>4</sub>, evaporate off the light petroleum and weigh the residue. Dissolve the fatty acids in light petroleum previously saturated with tetrabromostearic acid (III), cool to -4° C and add a solution (also cooled to -4° C) of bromine (5 ml) in light petroleum saturated with III (100 ml), dropwise, until a permanent yellow colour remains. Set the mixture aside overnight at 0° C, filter off the ppt., wash it with light petroleum saturated with III, dry and weigh.

P. S. STROSS

**3498. Separation of saturated straight-chain fatty acids. Qualitative paper-chromatography.** O. Perilä (*Acta Chem. Scand.*, 1955, **9** [5], 864-865).—Paper-chromatographic procedures for separating saturated straight-chain fatty acids from formic to

cerotic acid in separate are separate method (*Br*) saturated chromatography is used for dyeing with Formic and using AgNO<sub>3</sub> these meth detected. by Holasek 330), using methanol - acids migrat weight 90 g 0.05 mg of are detecte (0.01 mg of reversed-ph numbered and Nitsch is first sat 190° to 220 acetic acid acids from Of the odd acids were from ever numbered this group n-decoic t behenic to acids were n-decoic t After the paper, the converting locating th

**3499. A** S. David 1955, [6], graphy of hydrochri salts in quantity much giv prevents butyric ac observed. acids are  $\beta$ -phenyl are purifi silica gel (1:1). V column (c) is extru az-dimeth  $\beta$ -phenyl

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cerotic acid are described. The acids are analysed in separate groups. Those from formic to *n*-hexoic are separated as their ammonium salts by Hiscox's method (*Brit. Abstr. C*, 1951, 252), using *n*-butanol saturated with water as solvent. Rutter's circular chromatography method (*Brit. Abstr. C*, 1949, 434) is used for the elution. Acids are detected by dyeing with methyl red-bromothymol blue. Formic and acetic acids must be distinguished by using  $\text{AgNO}_3$ , which is reduced by formic acid. By these methods 0.05 mg of acid can be readily detected. *n*-Hexoic to *n*-decoic acids are separated by Holasek's method (*Angew. Chem.*, 1954, 66, 330), using as solvent carbon tetrachloride-methanol-conc. aq.  $\text{NH}_3$  soln. (81:18:1, v/v); the acids migrate as ammonium salts. If a paper of weight 90 g per sq. metre is used, not more than 0.05 mg of each acid can be separated. The acids are detected with a solution of rhodamine B; (0.01 mg of acid is still detectable). In Kaufmann's reversed-phase method for separating even-numbered acids, from *n*-decoic to stearic (Kaufmann and Nitsch, *Anal. Abstr.*, 1955, 2, 2557), the paper is first saturated with hydrocarbon (boiling range 190° to 220° C) and the elution is carried out with acetic acid-water (9:1, v/v). All even-numbered acids from *n*-decoic to cerotic acid were separated. Of the odd-numbered acids, *n*-nonoic and undecoic acids were separated easily from each other and from even-numbered acids. When both even-numbered and odd-numbered acids were present, this group was further divided into the groups *n*-decoic to palmitic, palmitic to behenic, and behenic to cerotic acids. When only even-numbered acids were present, the group was subdivided into *n*-decoic to stearic, and stearic to cerotic acids. After the hydrocarbon was evaporated from the paper, the acids (e.g., 0.1 mg) were detected by converting them into their copper salts and then locating the copper as the ferrous cyanide complex.

O. M. WHITTON

**3499. Analytical study of a mixture of fatty acids.** S. David and J. Monnier (*Bull. Soc. Chim. France*, 1955, [6], 797-798).—Paper partition chromatography of fatty acids from the oxidation of hexahydrochinaline is effected with the ethylamine salts in 0.005 *N* ethylamine in butanol. The quantity of ethylamine is somewhat critical as too much gives a background colour and too little prevents migration. Spots of acetic acid, *iso*-butyric acid, *isovaleric* acid and a  $\text{C}_6$  acid are observed. For chromatography on silica gel, the acids are neutralised with  $\text{Na}_2\text{CO}_3$  and treated with *p*-phenylphenacyl bromide. The esters formed are purified and chromatographed on a column of silica gel in a mixture of benzene and light petroleum (1:1). When the products are separated on the column (detected by ultra-violet light), the column is extruded and cut up. *isovaleric* acid and  $\alpha$ -dimethylbutyric acid are identified as their *p*-phenylphenacyl esters.

E. J. H. BIRCH

**3500. Column partition chromatography and its application to the separation of fatty acids.** E. Vioque (*Grasas y Aceites*, 1955, 6 [2], 88-93).—The separation of fatty acids by inverse-phase partition chromatography and by gas-phase chromatography is described.

L. A. O'NEILL

**3501. The chemical determination of vitamin D with special reference to its application to ultra-violet-irradiated yeasts. II. The chromatographic purification of solutions of vitamins  $\text{D}_2$  and  $\text{D}_3$  with**

**Floridin earth (60 to 90 mesh).** E. E. Bruchmann *Brantweinwirtschaft*, 1954, 76 [1], 184-185).—Before estimating vitamin  $\text{D}_2$  (ergocalciferol) in irradiated yeast and vitamin  $\text{D}_3$  (cholecalciferol) in cod-liver oil, tachysterol and vitamin A, respectively, must first be removed. The possibility of effecting this by chromatography on activated Floridin earth was examined. The optimum recovery (87.4 per cent. for vitamin  $\text{D}_2$  and 97.0 per cent. for  $\text{D}_3$ ) was obtained by activating the earth by boiling with HCl for 20 min. and eluting the vitamins with 90 per cent. alcohol. For complete separation of vitamins  $\text{D}_2$  and A, the mixture had to be chromatographed twice, giving a recovery of 75 per cent.

K. J. GARDNER

**3502. Circular paper chromatographic method for estimation of thiamine and riboflavin in multi-vitamin preparations.** K. V. Giri and S. Balakrishnan (*Anal. Chem.*, 1955, 27 [7], 1178-1180).—Mixtures of thiamine and riboflavin (up to  $\approx 4.5 \mu\text{g}$  in 11.2  $\mu\text{l}$  of solution) from standards and preparations are spotted on to a circular filter-paper and the spots (while still wet) are exposed to the vapour of BrCN and ammonia, oxidising the thiamine to thiochrome. The paper chromatogram is developed with a butanol-acetic acid-water solvent, and the spots formed (detected by their fluorescence) are eluted and determined quantitatively in a fluorimeter. The stability is shown to be satisfactory and the reproducibility of the method is  $\approx \pm 10$  per cent.

E. J. H. BIRCH

**3503. Determination of riboflavin by light absorption and polarographic methods.** A. J. Zimmer and C. L. Huyck (*J. Amer. Pharm. Ass., Sci. Ed.*, 1955, 44 [6], 344-348).—Spectrophotometric and polarographic methods are used to construct calibration curves in the visible and u.v. regions with U.S.P. riboflavin as a standard, and the results show both methods to be rapid and precise. Determination of riboflavin in tablets is achieved by weighing the equivalent of one tablet from a mixed sample, warming with 30 to 40 ml of 0.02 *N* acetic acid (if starch is present the temp. should not exceed 50° C) and filtering. The paper is washed until no fluorescence is detected in u.v. light. The soln. is diluted to 5  $\mu\text{g}$  of riboflavin per ml with 0.02 *N* acetic acid and the absorption is determined; when compared with the fluorimetric method, the results with visible light show better agreement than those with u.v. light. In the polarographic method it is not necessary to remove the tablet debris. Each determination takes about one hour. It is suggested that the standard curve at 270  $\mu\text{m}$  be used for the u.v. region. Both methods require a higher concn. of riboflavin than the fluorimetric method, e.g., the spectrophotometric method requires 2 to 5  $\mu\text{g}$  per ml and the polarographic method requires 10 to 100  $\mu\text{g}$  per ml. The effect of light is negligible in soln. containing 2  $\mu\text{g}$  of riboflavin per ml in 0.02 *N* acetic acid at a pH of 3.4.

G. R. WHALLEY

**3504. Assay of ascorbic acid in rose-hip extract by paper chromatography.** B. Johannesen (*Pharm. Acta Helv.*, 1955, 30 [1], 22-33).—A quant. method is given for the assay of ascorbic acid (I) in extract of *Rosa canina* fruit, based on paper chromatography followed by colorimetry according to Schmall et al. (*Anal. Abstr.*, 1954, 1, 370). Sugars do not interfere, and dehydroascorbic acid is not assayed unless first reduced by  $\text{H}_2\text{S}$ . Results are about 10 per cent. lower than those given by the

method of Schmall or by titration with iodine. *Procedure*—Apply a soln. of the sample in 10 per cent. acetic acid (10  $\mu$ l containing  $\approx$  50  $\mu$ g of **I**) to Whatman No. 1 paper and, after 6 hr., develop with *n*-butanol - water - acetic acid (10:3:2) for 14 hr. Dry, and elute the **I** zone with 5 ml of an aq. ethanolic soln. of diazotised 4-methoxy-2-nitroaniline (*cf.* Schmall, *Ibid.*). After 3 min., add 6 per cent. NaOH soln. (2 ml) and compare the extinction at 570  $m\mu$  with that of a blank soln.

A. R. ROGERS

**3505. The determination of tocopherols by paper chromatography.** J. Green, S. Marcinkiewicz and P. R. Watt (*J. Sci. Food Agric.*, 1955, **6** [5], 274-281).—Methods given for determining individual tocopherols in natural oils and foodstuffs are based on either a single-dimensional separation on ZnCO<sub>3</sub>-impregnated paper, or this separation in conjunction with a two-dimensional partition separation on paraffin-coated paper. Chromatographic runs are short and rapid and can be made without preliminary removal of carotenoids and moderate amounts of vitamin A or sterols. Over 98 per cent. recoveries are obtained with pure tocopherols. The presence of the recently described 5-methyltocol in wheat products has been confirmed and, in addition, with two-dimensional methods, a substance has been isolated from some cereal grains which appears to be a new tocopherol.

O. M. WHITTON

See also Abstracts 3377.

#### Sanitation

**3506. "Oxygen absorbed" from acid permanganate in the presence of chloride.** R. F. Roberts (*Analyst*, 1955, **80**, 517-519).—When chlorides are present in samples of sewage or industrial effluents examined by the "oxygen absorbed" test, results are frequently high. This is shown to be due not to loss of Cl but probably to reaction between the Cl and some organic substances. This interference can be reduced to a negligible amount by the use of dil. H<sub>3</sub>PO<sub>4</sub> (1 + 3) instead of the dil. H<sub>2</sub>SO<sub>4</sub> usually employed. With this change the technique of the method is that described in "Methods of Chemical Analysis as Applied to Sewage and Sewage Effluents," Ministry of Health, H.M. Stationery Office, 1929, p. 28.

A. O. JONES

**3507. Gasometric determination of dissolved oxygen in pure and saline water as a check of titrimetric methods.** A. B. Wheatland and L. J. Smith (*J. Appl. Chem.*, 1955, **5** [3], 144-148).—The gasometric method described for the determination of dissolved oxygen consists in extracting dissolved gases from a known volume of water by boiling under vacuum, followed by measurement of the volume and composition of the extracted gases in a constant-volume gas-analysis unit. This apparatus gives results within 0.05 p.p.m. of the correct value. Determination of dissolved oxygen by this method and by the Winkler titration method for distilled water, and by the azide modification of the Winkler method for sea water, gave values which agreed within the limits of experimental error.

O. M. WHITTON

**3508. The detection of barium and strontium in water analysis.** K.-E. Quentin (*Z. Lebensmitt.-Untersuch.*, 1954, **99** [2], 85-90).—Small amounts of Ba and Sr in natural waters are detected after separation and enrichment by cation-exchange resins, *e.g.*, equal wt. of Lewatit S 100 and Permutit

RS; 30 to 40 g of resin generally suffice for 1 litre of water. Interfering substances such as HBO<sub>3</sub> and H<sub>2</sub>SiO<sub>3</sub> are removed and the Ca, Sr and Ba are eluted consecutively from the column by 10 per cent. HCl, in higher concn., which may be determined gravimetrically as oxalate or sulphate (amounts > 5 mg) or volumetrically with EDTA (amounts > 0.5 mg). Detection and separation of Ba (> 0.5  $\mu$ g) and Sr (> 3  $\mu$ g) from the eluates by paper chromatography with sodium rhodizonate are described in detail; comparison of the colours given by standard solutions permits semi-quant. determination of Ba and Sr in amounts < 0.5 mg to an accuracy of  $\pm$ 20 per cent.

D. R. GLASSON

**3509. Factors affecting the determination of fluoride in water with zirconium - alizarin.** W. L. Lamar and P. G. Drake (*J. Amer. Wat. Wks. Ass.*, 1955, **47** [6], 563-572).—The colorimetric determination of fluorides by the Zr - alizarin reaction is reviewed. The preparation of standards is specified and the interferences due to other substances are considered. A correction factor is evolved to overcome interference effects from Al. Free Cl causes errors and it should therefore be removed. Interference by phosphates is complex and no correction procedure appears to be feasible; if the phosphate in the sample aliquot exceeds 0.20 mg, the fluoride should be isolated by distillation as H<sub>2</sub>SiF<sub>6</sub>. Full details of the distillation apparatus and procedure are given.

S.C.I. ABSTR.

**3510. Use of permanent standards in fluoride analysis [of water].** R. E. Frazier (*J. Amer. Wat. Wks. Ass.*, 1955, **47** [6], 560-562).—The use of portable field kits for testing the fluorine content of water supplies, their limitations and the precautions to be observed are discussed, with particular reference to the reliability of permanent colour standards. The basis of the test is the colour developed in the presence of F<sup>-</sup> as a result of their action in decolorising the red lake formed by Zr and alizarin in a solution of a certain acidity. It is considered that comparators with permanent standards, if correctly used, can give results which are accurate within 0.2 p.p.m. of fluoride. Polyphosphates, or the presence of alum or aluminates, interfere with the determination and it may then become necessary to use a distillation procedure.

S.C.I. ABSTR.

**3511. The colorimetric determination of lead in effluents.** E. J. Serfass and R. M. Muraca (*Plating*, 1955, **42** [6], 751-754).—The method consists in extracting the reduced effluent with dithizone soln. at pH 2 to 3 to remove interfering elements, particularly bismuth and tin. A subsequent extraction at pH 8 to 9 in the presence of cyanide removes the lead as dithizonate. After removing the excess of dithizone by extraction at pH 11.5 the intensity of colour of the Pb dithizonate is determined by means of a colorimeter or spectrophotometer. The sample is first fumed with H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> to remove organic matter and then reduced with hydrazine to lower the oxidation state of those elements that can oxidise dithizone. The method is sensitive to 50  $\mu$ g of Pb per ml.

N. E.

**3512. Determination of hexachlorocyclohexane (HCH) in the presence of DDT in insecticide powders.** K. H. Wummel (*Chem. Tech., Berlin*, 1954, **6** [7], 382-383).—The powder is extracted with ether or acetone and 0.3 to 0.6 g of dried extract is heated on a water bath with 15 ml of fuming sulphuric acid (20 to 25 per cent. SO<sub>3</sub> content). The DDT is

thus converted into water-soluble sulphur compounds without affecting the HCH. The resulting solution is diluted with  $H_2SO_4$  and water, the HCH is extracted with benzene and decomposed by boiling with  $N$  KOH (methanolic). The chlorine is determined with  $0.1\ N$   $AgNO_3$ . Full experimental details are given. The DDT can be determined by omitting the treatment with fuming sulphuric acid, obtaining the total chlorine content, and subtracting the chlorine found for the HCH.

K. J. GARDNER

See also Abstracts 3350, 3490.

#### Agriculture and Plant Biochemistry

**3513. Spectrographic analysis of trace elements in plant materials. A comparison between the anode arc and cathode-layer arc methods of excitation.** A. Strasheim and L. Camerer (*J. S. Afr. Chem. Inst.*, 1955, **8** [1], 28-38).—The relative merits of the cathode and anode methods of excitation for the spectrochemical analysis of trace-element oxide concentrates (particularly Ni, Co, Mo, Sn, Pb, Ti, V and Cr) are compared. The accuracies attainable by the two methods are about the same and the alignment of the anode is less critical than that of the cathode. The cathode method is more suitable for the determination of Co and Mo.

A. JOBLING

**3514. Determination of copper in plant materials by means of zinc dibenzylthiocarbamate.** S. Andrus (*Analyst*, 1955, **80**, 514-516).—A method is described for the rapid absorptiometric determination of Cu (up to 15 p.p.m.) in plant materials. The sample (2 g) is wet-ashed with  $H_2SO_4$ ,  $HNO_3$  and  $HClO_4$ , and the diluted digest is extracted with a 0.01 per cent. soln. of zinc dibenzylthiocarbamate in  $CCl_4$ . The optical density of the yellow extract is measured at 440  $m\mu$  against a blank soln. The copper content is determined from a calibration graph prepared by extracting dilutions of a standard soln. of  $CuSO_4$  acidified with  $H_2SO_4$  with the reagent. Recovery is good and there is no interference from other metals commonly occurring in plant material.

A. O. JONES

**3515. Volumetric determination of fluorine [in plants, soil, etc.] involving distillation from a sulphuric acid solution.** O. D. Smith and T. D. Parks (*Anal. Chem.*, 1955, **27** [6], 998-1000).—The use of  $H_2SO_4$  and distillation at  $150^\circ C$  in the Willard and Winter method decreases the retarding influence of Al and Si on the volatilisation of fluorides in the analysis of vegetation, soil and particulate materials. A modified steam-tube minimises contamination of the distillate. In the procedure given for fluorine in vegetation, a reagent blank is included with each group of samples. Moisture is determined on a separate sample. To a 10 to 15-g sample in a nickel dish,  $MgO$  is added in the ratio of 1 g of  $MgO$  to 30 g of sample. The solid is covered with water and mixed, and the alkalinity is tested. An alkaline condition is maintained by adding more  $MgO$  while evaporating to dryness. The dried sample is ashed with access to air, starting at  $300^\circ C$  and gradually increasing to  $600^\circ C$  until the ash is pale grey. The ash and 10 g of NaOH are heated in a 200-ml Inconel dish for 5 to 10 min. at  $600^\circ C$ , the ash being mixed with the melt. The fused product is cooled, 50 ml of water are added, and disintegration is effected by boiling for 20 to 30 min. After the addition of

sufficient  $Ag_2SO_4$  to precipitate the chlorides present, and 60 ml of  $24\ N$   $H_2SO_4$ , the product is first distilled up to  $145^\circ C$  and then steam-distilled at  $145^\circ$  to  $155^\circ C$ ; 500 ml of distillate are collected during 2 to 3 hr. The standardisation of the thorium nitrate solution and its use in determining the fluorine in the sample are described.

O. M. WHITTON

**3516. Flame-photometric determination of calcium, magnesium and manganese in plant ash and soil extracts.** H. Kick (*Z. PflErnähr. Düng.*, 1954, **67** [1], 53-57).—A simple elimination of the interference of  $Al^{+++}$  and  $PO_4^{---}$  in the flame-photometric determination of Ca is described. Aliquot portions (30 ml) of the solution of the ash in  $HNO_3$ , containing  $< 120$  mg of Ca per 100 ml, are boiled with 10 ml of  $0.1\ N$   $AlCl_3$ , neutralised with carbonate-free aq.  $NH_3$  to methyl red, cooled and treated with 10 per cent. ammonium acetate to give a total vol. of 100 ml. The  $Al^{+++}$  and  $PO_4^{---}$  are then almost completely removed by filtration. The Mg and Mn are determined by flame photometry in the presence of Fe and K after preliminary separation as  $MgNH_4PO_4$  and  $MnNH_4PO_4$ . *Procedure*.—Portions of test soln. (100 ml, containing  $< 100$  mg of  $MgO$ , 30 mg of  $MnO$  and 20 mg of  $Fe_2O_3$ ) in dilute ( $< 2\ N$ )  $HCl$  or  $HNO_3$  heated to  $90^\circ$  to  $95^\circ C$  are treated with 25 ml of tartaric acid (500 g per litre), 10 ml of  $(NH_4)_2HPO_4$  (75 g per litre) and 25 ml of 25 per cent. aq.  $NH_3$ ; the mixture is boiled for 1 to 2 min. and set aside for 1 hr., the ppt. is filtered off, dissolved in 5 ml of  $HNO_3$  (sp. gr. 1.2) or 10 per cent.  $HCl$  and the solution is diluted to 100 ml. A monochromator instead of a filter may be used for the flame-photometric measurements at 285  $m\mu$  or, more sensitively, at 371  $m\mu$  for Mg and at 403  $m\mu$  for Mn. For the determination of Mg and Mn, 2 to 5 g and  $\approx 20$  g, respectively, of plant material are required, if amounts of  $< 1$  mg per 100 g are to be estimated.

D. R. GLASSON

**3517. Determination of methoxyl in lignified substances.** K. Kürschner and T. Schweizpacher (*Faserforsch. u. Textiltech.*, 1955, **6** [4], 157-163).—The method for the determination of methoxyl in lignified substances (*Ibid.*, 1953, **4**, 287, 507) has been modified. The technique, applied to solid lignified substances, lignin-sulphonic acids (Ca lignosulphonate) and liquids containing methoxyl groups, is described in great detail with an additional extension of the method to analyses of wood hydrolysates, condensates, dialysates, etc.

S.C.I. ABSTR.

**3518. Studies of soil manganese. I. The use of disodium calcium Versenate for the extraction of bivalent manganese from soils.** R. S. Beckwith (*Aust. J. Agric. Res.*, 1955, **6** [2], 299-307).—Bivalent manganese in soils can be extracted at pH 8.0 with a buffer of calcium and ammonium acetates containing 1 per cent. of disodium calcium EDTA. Hausmannite, manganite, and manganous manganite were not attacked by the extractant even in the presence of soils. Bivalent manganese formed by treatment of soils with reducing agents can also be extracted. The periodate method was used for the manganese analyses reported, after destroying all extracted organic matter with  $HNO_3$  and  $HClO_4$ . Preliminary results with three ptd. oxides indicate that the degree of attack by quinol in the presence of the new extractant at pH 8 reflects the availability of these oxides to oats grown on fen soil. Some applications of the new reagent are briefly discussed.

O. M. WHITTON

**3519. The determination of antibiotic content in supplemented feeding-stuff.** S. J. Edwards and M. D. Haskins (*J. Sci. Food Agric.*, 1955, **6** [4], 218-223).—The microbiological assay of penicillin and aureomycin in supplemented pig-food by the tube serial-dilution and the paper-disc methods has been studied. In the serial-dilution test, an aq. extract of the meal is prepared, and the concn. is determined by comparing its inhibitory end-point with that of extracts from standard control meals containing known amounts of antibiotic; it is shown that a narrow range of concn. can be assigned to the sample meal, and that the test is not subject to interference by non-specific substances in the meal. The paper-disc method, which involves extraction with 95 per cent. methanol followed by plate assay, provides a single reasonably accurate value of concn., but the technique is more difficult.

A. R. ROGERS

See also Abstract 3395, 3420.

## 5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

### General

**3520. Note on the filtration of difficultly filterable precipitates.** R. Pietsch (*Mikrochim. Acta*, 1955, [4], 859-863).—A method of filtering, involving mechanical stirring of the liquid in the filtering vessel, is described. The procedure accelerates the filtration of solutions containing flocculent or gelatinous ppt. such as certain hydroxides.

W. J. BAKER

**3521. A sensitive optically recording mechanical balance.** H. Zieske, jun., T. D. Bair and M. N. Levy (*Proc. Soc. Exp. Biol. Med.*, 1955, **88**, 641-643).—A sensitive mechanical balance, which optically records the stress exerted on a flat spring by means of two obliquely orientated plane mirrors, is described. A vertically directed strain on the spring is registered as a horizontal deflection of a line of light at the camera aperture. Sensitivity and frequency may be easily varied to meet changing requirements. An example to demonstrate the use of the balance as a flow meter in perfusion studies on isolated tissues is described. V. M. WOOTTON

**3522. Manual apparatus for determining moisture in gases, and its use.** M. S. Maslenikov (*Zavod. Lab.*, 1955, **21** [3], 371-373).—An apparatus, whose use is based on the measurement of a dew-point and of pressures at different temp., is described.

G. S. SMITH

**3523. An all-glass laboratory still.** D. Simmonite and M. G. Williams (*Pharm. J.*, 1955, **175**, 31-32).—A still, constructed from Pyrex glass, comprises an electrolytic boiler assembly with electrodes (carbon rods  $\frac{3}{8}$  in. in diameter), a series of concentric tubes which function as a baffle, and a double-surface condenser. For an electrical consumption of 750 W, an output of  $\approx 1000$  to 1200 ml of distilled water per hr., pyrogen-free and conforming to B.P. requirements for injection purposes, is obtained.

S.C.I. ABSTR.

**3524. A jacketed extraction apparatus.** G. Keil (*Chem. Tech., Berlin*, 1954, **6** [10], 551-552).—The jacketed extraction apparatus described provides temp. control of the solvent vapour and of the flow-liquid in the condenser. After extraction, the solvent is readily removed from the

residue by vaporisation while the flow of liquid in the condenser is stopped. A jacketed percolator is also described. Both sets of apparatus are applicable to extraction of waxes, oils, fats and asphalts.

D. R. GLASSON

**3525. Investigations on extraction columns.** A. Guyer, A. Guyer, jun., and K. Meuli (*Helv. Chim. Acta*, 1955, **38** [3], 790-797).—Numerous investigations have been made on the extraction and the exchange of material between two liquid phases and the method of using individual types of extraction apparatus, but with the introduction of extraction columns with mechanical mixing of the phases the need has arisen for characterising the mode of action of the extraction apparatus. By using the system carbon tetrachloride - water-benzoic acid, the behaviour of three types of liquid-liquid extraction columns (Scheibel's, a new "Vibro" and a "Fülkörper" column) has been studied within the limits of their working range. Particular attention has been paid to determining the dependence of the extraction-efficiency and of the "hold up" [i.e., ratio of vol. of disperse phase to vol. of the empty column (per cent.)] on the rate of flow of both phases while the column is mechanically stirred under previously determined optimal rates of stirring. A new method of presenting the characterising factors of various types of column has been devised which shows clearly the different behaviour of the same type under various working conditions and renders it possible to make appropriate comparisons.

P. HAAS

**3526. Acetylation of chromatographic paper.** J. W. H. Zijp (*Chem. Weekbl.*, 1955, **51** [30], 547-548).—A simple method for the complete acetylation of chromatographic paper is described. The paper, in rolls, is soaked in glacial acetic acid and then treated with an acetylating mixture consisting of 350 ml of acetic anhydride, 435 ml of glacial acetic acid, 1000 ml of toluene and 0.8 ml of 70 per cent.  $\text{HClO}_4$ . The fibrous structure of the paper is not destroyed by this method.

A. J. MEE

**3527. New arrangement for capillary elution in paper chromatography.** C. Dumazert and M. Bozzi-Tichadou (*Bull. Soc. Chim. Biol.*, 1955, **37** [1], 169-170).—A new and improved design of the apparatus described earlier (*Anal. Abstr.*, 1955, **2**, 3445) is illustrated. The method allows for a more rapid elution, and the use of a very small vol. of liquid. The necessity for working in a saturated atmosphere, unless the eluting agent is very volatile, is avoided.

P. HAAS

**3528. Apparatus for continuous chromatographic separation.** H. Svensson, C.-E. Agrell, S.-O. Dehlén and L. Hagdahl (*Sci. Tools*, 1955, **2** [2], 17-21).—A rotating composite column (I) consists of 36 glass tubes ( $11 \pm 0.1$  mm internal diameter), each packed with sorbent, arranged regularly round the periphery of a cylinder and held in position by a perforated brass sheet and ring. The sample liquid and eluting solvent (II) are proportioned by a liquid flow distributor, comprising a cylindrical block rotating at the same rate as I, and with 36 conical and overlapping holes spaced equidistantly round a circle of the same radius as the more rapidly rotating orifice of a Mariotte flask containing II. An escape-tube arrangement prevents II from entering the column that, at any given moment, is receiving sample solution. A

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flow distributor, which does not rotate, at the base of the composite cylinder, carries each fraction of a component to each of a set of 36 100-ml flasks. Preliminary sorption tests with a particular sample are required to determine precise operating conditions. S.C.I. ABSTR.

See also Abstracts 3373, 3397, 3402, 3445.

### Optical

**3529. X-ray emission spectrography using ion-exchange membranes.** W. T. Grubb and P. D. Zemany (*Nature*, 1955, **176**, 221).—The spot-test technique of X-ray emission spectrography has been extended to lower concn. of metal ions by using ion-exchange resin membranes to concentrate the elements present as ions in dilute solutions, and to act as a carrier for the sample in the spectrograph. The method is best suited to analysis at high dilution. The extraction of  $1 \mu\text{g}$  of  $\text{Co}^{++}$  from a litre of solution, with an error of  $\pm 0.1 \mu\text{g}$ , and the extraction of  $0.5 \mu\text{g}$  each of Zn and Mn together with  $1 \mu\text{g}$  of Fe from 100 ml of maple syrup diluted to 1 litre, are given as examples.

K. A. PROCTOR

**3530. Application of X-ray quantumeters in analysis.** E. Lüscher (*Mikrochim. Acta*, 1955, [2-3], 696-702).—The most important work in the range of X-ray emission spectrography and the basic construction of the X-ray quantumeter are described. The spectral range for dispersive measurements is from 0.6 to 3.1 Å. Geiger-Müller and scintillation counters serve as energy detectors, and plain and cylindric mono-crystals are used as analysers. A determination of Pb and Br in benzene is made by using the non-dispersive arrangement.

D. R. GLASSON

**3531. X-ray photo-electron spectrometer with electrostatic deflection.** R. G. Steinhardt, jun., F. A. D. Granados and G. I. Post (*Anal. Chem.*, 1955, **27** [7], 1046-1050).—Replacement of the magnetic analyser by a radial ( $127^\circ 17'$  deflection), inverse first-power electrostatic-field analyser has considerably improved the performance of the X-ray photo-electron spectrometer used for the chemical analysis of surfaces and sub-surface regions of solids. Resolution is increased five-fold,  $\Delta E/E$  being variable from  $\approx 0.003$  to  $0.025$ ; the inherent intensity is increased by a factor of  $\approx 20$ , whilst single determinations of energy values are accurate to  $\pm 0.1$  per cent, and can be effected in  $< 10$  min. By mounting as many as 48 samples on a rotating drum any specific sample can quickly be analysed without opening the chamber to the air. The theory, design and construction of the instrument are described, whilst its operating characteristics are exemplified by the X-ray photo-electron spectra of pure Au and Rh obtained at different resolutions. Since this electrostatic analyser can measure the  $\text{MoK}_{\alpha_1}$ - $\text{MoK}_{\alpha_2}$  separation with an accuracy of  $\approx 0.5$  per cent., further improvement in resolution will not increase its utility in chemical analyses.

W. J. BAKER

**3532. Miniature fluorescent X-ray spectrograph.** L. S. Birks and E. J. Brooks (*Anal. Chem.*, 1955, **27** [7], 1147-1149).—The construction and operation of a small, inexpensive X-ray spectrograph with no moving parts and with means for recording spectra from two specimens simultaneously, side by side,

on photographic film, are described. It is easily adapted to a tungsten-target X-ray diffraction tube operated at 50 kV and 20 mA with exposures of 0.5 to 1 hr. LiF is the preferred analysing crystal for  $\lambda \approx 0.50 \text{ Å}$  and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  for elements from  $^{28}\text{Si}$  to  $^{52}\text{Cr}$ . The instrument can be used for qual. and semi-quant. analysis; concn. of 2 per cent. of Mn in an iron matrix and of  $< 0.5$  per cent. of Mn in an aluminium matrix can be detected. Resolution is adequate to separate the  $\text{MnK}_{\alpha}$  line at  $2.10 \text{ Å}$  from the  $\text{CrK}_{\beta}$  line at  $2.08 \text{ Å}$ . W. J. BAKER

**3533. Multichannel instruments for fluorescent X-ray spectroscopy.** J. W. Kemp, M. F. Hasler, J. L. Jones and L. Zeitz (*Spectrochim. Acta*, 1955, **7** [3], 141-148).—Two multichannel instruments for fluorescent X-ray spectroscopy are described in detail. They are not suitable for the analysis of low concn. of elements of atomic number  $< 20$ , and the limits of detectability for other elements are a function of the base material as well as of the various instrumental factors involved, and vary from 1 p.p.m. to several thousand p.p.m. When sufficient intensity can be provided (e.g., by the use of curved crystals or non-dispersive techniques) to allow the use of scintillators, then coefficients of variation of 0.1 to 0.5 per cent. can be expected. The electronics used have been shown to give standard deviations of intensity ratios of  $\approx 0.2$  per cent. K. A. PROCTOR

**3534. Methods of introducing the sample into the light source in spectrographic analysis.** T. K. Aldarov (*Zavod. Lab.*, 1955, **21** [3], 366-367).—In the analysis of solutions, an aluminium electrode, pre-sparked to give some porosity, can replace the carbon electrode when the CN bands are undesirable. A moving electrode is described for introducing powders and solutions into the arc. As an alternative to briquetting, a powdered sample may be mixed with an alcoholic solution of bakelite lacquer on a copper plate, which will serve as an electrode for spark excitation. G. S. SMITH

**3535. Removal of the porosity of carbon electrodes used for spectrographic analysis of solutions.** Kh. I. Zil'bershtein and L. P. Makarov (*Zavod. Lab.*, 1955, **21** [3], 342-344).—The effectiveness of various substances, kerosene, cellulose nitrate, wax, paraffin, and 3.5 per cent. polystyrene in benzene, in reducing the porosity of carbon electrodes is studied by examining the depth of penetration of solutions into the carbon by means of X-rays. The most effective material is polystyrene. G. S. SMITH

**3536. A contribution to solution spectrum analysis.** H. Svejda (*Mikrochim. Acta*, 1955, [2-3], 251-256).—A cup-disc metal electrode is devised for sparking-off solutions from a Petrey holder. This electrode, when used with a newly developed holder, affords greater speed and better sensitivity in solution spectrum analysis. D. R. GLASSON

**3537. Recent advances in direct-reading spectroscopic analysis.** A. C. Menzies and J. Skinner (*Mikrochim. Acta*, 1955, [2-3], 614-629).—Two new instruments, viz, a 3-m-grating polychromator and an attachment to the medium quartz spectrograph, are described. Basic considerations in their design include the alternative uses of scanning systems or fixed slits and of gratings or prisms. The outstandingly great advantages of the time and integration factors favour the polychromator

method. The 3-m-grating instrument has electronics suitable for use with 30 EMI-type electron multipliers. Spectral lines down to wavelengths of  $194\text{ m}\mu$  can be used. Automatic temp. compensation is provided. The charges are integrated on condensers and the potentials acquired are measured by a counting technique, with a quartz-crystal oscillator for timing; the no. of oscillations occurring while a highly stabilised direct current charges condensers linearly to potentials of the integrating condensers are shown on a 4-stage dekatron counter and are simultaneously printed on a paper strip. The medium quartz spectrographic attachment carries 11 electron multipliers. Currents from these charge condensers, the potentials being measured with a balanced valve voltmeter. Display is made on a microammeter with a pen recorder in parallel if desired. Indications of the analytical precision are obtained from analyses of flat samples of aluminium casting alloy and of Mg, and of the additives Ba, Ca, and Zn in lubricating oil in concn. 0.015 to 0.5 per cent.; in the analysis of the oil, the intermittent a.c. arc is used between a graphite counter-electrode and wheel, turning while dipping in a dish, slits being set on appropriate lines of the four elements and the ratio taken against the background of the arc.

D. R. GLASSON

**3538. Quantitative spectrographic analysis by means of the "stelescope."** A. M. Borbat, M. S. Soskin and S. G. Finkel'shtein (*Zavod. Lab.*, 1955, **21** [3], 313-316).—The electro-erosion method (Sventitskii and Taganov, *Ibid.*, 1947, **13**), which has two stages, (i) transfer of the material from the sample by means of the arc to one electrode, and (ii) evaporation of the transferred material in an arc between the first electrode and a second new electrode, is applied to the analysis of steel and copper alloys by means of the "stelescope." Under standard conditions, the time of burning of the arc is a measure of the concn. of the element being determined. Calibration curves are plotted with time in sec. and percentage concn. as co-ordinates. The time of burning of the arc is taken to be the moment of attainment of equivalence of intensity of a line with that of a comparison line. A special disc electrode is described.

G. S. SMITH

**3539. Use of the "stelescope" for semi-quantitative spectrographic analysis of mixtures of gases.** O. P. Bochkova and E. Ya. Shreider (*Zavod. Lab.*, 1955, **21** [3], 311-312).—Contents of from 0.001 to 1 per cent. of Ne in He are determined by creating in a quartz tube containing the gases a discharge between external electrodes, and observing the relative intensities of the lines Ne 6402 Å and He 6678 Å with a seven-step sector.

G. S. SMITH

**3540. The use of intensity scales in the microphotometry of spectra.** J. McK. Nobbs and P. T. Beale (*Spectrochim. Acta*, 1955, **7** [3], 165-174).—A description is given of the construction and application of intensity scales for use in a Hilger galvoscale projector, by means of which the conversion of linear galvanometer deflections to relative intensities is carried out in the microphotometer concurrently with the initial line measurements. The scales are drawn empirically from plate calibration curves of relative intensity *vs.* linear galvanometer deflection, and their construction involves photographic reduction of the original drawing and slight modification of the galvoscale projector. If

plates of varying contrast factor are used, a family of scales is required to cover the range of contrast expected for the type of plates and developing conditions employed. To facilitate the drawing of the plate calibration curves, graph paper incorporating a modified logarithmic scale (Partial Siedel Transformation) is used to extend the density range covered by a straight-line calibration curve. No difference was found between results obtained by the use of these scales and those obtained by the usual methods of plate evaluation, although it is emphasised that all possible care must be taken in assessing the characteristic angle for the plate, measurements to the nearest half degree being desirable. The method is particularly useful when background corrections are required.

K. A. PROCTOR

**3541. New sample holder for reflection measurements with the Beckman model DU spectrophotometer.** G. Tonnquist (*J. Opt. Soc. Amer.*, 1955, **45** [7], 582).—The sample holder described can be loaded with up to five samples, simultaneously. The sample size may be as large as  $5\text{ cm} \times 6\text{ cm}$  in area and 1.5 cm thick.

B. S. COOPER

**3542. Automatic photo-electric ultra-violet analyser for continuous chemical analysis of process streams.** L. G. Glasser (*J. Opt. Soc. Amer.*, 1955, **45** [7], 556-563).—The instrument described employs a double-beam system for measuring the absorption, at any selected wavelength between 220 and  $1200\text{ m}\mu$ , of a liquid or gas stream in a "flow through" cell. Radiation sources, isolating filters and photocells are interchangeable to provide various monochromatic radiations, or a simple monochromator may be attached. The measuring system uses the principle of optical balance in conjunction with a bridge-type photo-electric detector. The results may be fed to a suitable recorder. Substances that can be determined quantitatively by this method include nitrates, halogens, unsaturated hydrocarbons, ketones, benzene compounds, naphthalenes and anthraquinones.

B. S. COOPER

See also Abstracts 3283, 3284, 3363, 3513.

### Thermal

**3543. Calibration of temperature-measuring instruments.** Anon. (*Dep. Sci. Ind. Res. Nat. Phys. Lab. Notes Appl. Sci.*, No. 12, 1955, 47 pp.).—Methods for the realisation of the fixed points and the primary standards used at the National Physical Laboratory, *i.e.*, the instruments specified in the text of the International Temperature Scale for interpolation between the fixed points, *viz.* platinum resistance-thermometer ( $-182.97^\circ$  to  $+630.5^\circ\text{C}$ ), Pt/10 per cent. Rh - Pt thermocouple ( $630.5^\circ$  to  $1063^\circ\text{C}$ ), and disappearing-filament optical pyrometer with sectorised discs (for temp. above the Au pt.), are described, together with various working standards. The routine testing of liquid-in-glass thermometers, resistance thermometers, thermocouples, tungsten-strip lamps, and optical pyrometers, and the construction of comparison baths and furnaces are outlined. Standards of temp. are exceptionally liable to deterioration (which, even if it is slow, is none the less insidious) merely through usage. It is therefore desirable that users of temp.-measuring instruments should be equipped for making routine checks of accuracy.

J. M. JACOBS

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**3544. An all-glass rotary film evaporator.** M. E. Volk (*Anal. Chem.*, 1955, **27** [7], 1207).—In the device described and illustrated a rotating round-bottomed flask is connected to a lyophilising unit and thence to a vacuum-pump by a hollow glass-shaft and short adapter carrying a lubricated ball-joint. Only the hollow shaft and the flask rotate. As the axis of rotation is  $\approx 15^\circ$  from the horizontal, rather more than one-half of the vol. of the flask can be occupied safely by the soln. when the evaporation is started. The turbulence induced in the liquid effectively prevents bumping, whilst the lyophiliser acts as an efficient condenser and traps any radioactivity. Aqueous and ethanolic solutions in 2-litre flasks can be evaporated to dryness in 1 hr. W. J. BAKER

**3545. Air stirring in bomb calorimetry.** J. W. Whitaker, A. K. Ghosh and R. N. Chakravorty (*Fuel, Lond.*, 1955, **34** [3], 317-320).—A copper tube (0.375 in. in diameter), reaching to within 1 in. of the bottom of the vessel enclosing the bomb, is connected to a source of air or O which is bubbled through 500 ml of water and through a spray trap, unless a wet gas meter is used. The air is metered and a regular flow of 1 litre per min. is maintained. The lid of the calorimeter is replaced by a Perspex lid in which six holes are drilled to take the tube, a thermometer and the electrical connections, and to allow the air to escape. A reduction of errors arising from heat generated by a mechanical stirrer is effected. A. R. PEARSON

### Electrical

**3546. Analytical and micro-preparative carrier electrophoresis at high voltage.** T. Wieland and G. Pfeleiderer (*Angew. Chem.*, 1955, **67** [9-10], 257-260).—A full description is given of an apparatus and method for the analysis of mixtures, or the micro-preparation of substances from such mixtures, by electrophoresis at high (up to 3000) voltages, with a field of up to 60 V per cm. The paper or carrier (starch or cellulose powder) impregnated with the buffered solution of the test mixture is subjected to the charge in a damp chamber while lying on a glass plate, which is cooled to  $0^\circ$  to  $-5^\circ$  C by contact on the underside with a cooling fluid, and a Cellophane diaphragm (film) is interposed between the paper or carrier and the electrodes to permit passage of liquid while preventing endosmosis of the ions. Detailed and illustrated descriptions are given of a number of applications of the method. H. L. WHITEHEAD

**3547. Analysis with the electron polaroscope.** J. Heyrovský (*Anal. Chim. Acta*, 1955, **12** [6], 600-609).—The electron polaroscope is described. This instrument is used for oscillographic polarography with a.c., and yields diagrams of  $dV/dt$  plotted against V, where V is voltage and t is time. The method, which has been described previously (*Anal. Chim. Acta*, 1953, **8**, 283), is extended to the detection or determination of some local anaesthetics, sulphonamides, alkaloids, vitamins, antibiotics and phenobarbitone. W. C. JOHNSON

**3548. Thermostatically controlled polarographic electrolyser.** P. N. Tereshchenko (*Zavod. Lab.*, 1955, **21** [3], 370-371).—A new form of polarographic cell is described. G. S. SMITH

**3549. Potentiometric titrations using resin-membrane electrodes.** S. K. Sinha (*J. Indian Chem. Soc.*, 1955, **32** [1], 35-38).—The use of reversible resin-membrane electrodes, prepared from ion-exchange resins, in the potentiometric titrations of acid-base, chloride, and sulphate is described. IONAC C-200 and RF resins were used for titrating an HCl solution with an NaOH solution. A solution of 0.1 N HCl (10 ml), placed on the inner side of the membrane, was titrated with N alkali solution. A soln. of NaCl was titrated with a standard  $\text{AgNO}_3$  solution, using IONAC A-300 membrane electrodes, saturated with respect to  $\text{Cl}^-$ . Sulphate solutions were titrated against standard barium salt solutions, using Amberlite IRA-400 electrodes saturated with sulphate ions. Titration curves are presented and discussed. O. M. WHITTON

**3550. A colorimetric coulometer.** T. C. Franklin and C. C. Roth (*Anal. Chem.*, 1955, **27** [7], 1197-1199).—A coulometer having a range of  $> 10$  coulombs is made by modifying a clinical-type colorimeter (12-mm tube) so as to measure the change in colour in a soln. caused by an electrode reaction. The number of coulombs is obtained from the time of flow of a const. current through a galvanometer shunt system previously calibrated as a micro-ammeter. The most sensitive coulometer (0.01 to 1 coulomb) makes use of the reaction of  $\text{H}_2\text{O}$  at the cathode, the change in pH being determined colorimetrically with an acid-base indicator (0.1 to  $1 \times 10^{-4}$  M thymol blue or o-cresol red). A preliminary standardisation curve is necessary. The dissolution of Cu to the blue triethanolamine complex in a 28 per cent. triethanolamine soln. can also be used, but the sensitivity of the coulometer is limited to  $\approx 1$  to 10 coulombs. The direct reduction or oxidation of a coloured substance is not very satisfactory because of the tendency to pptn. on the electrode, although  $\text{KMnO}_4$  (reduced with 100 per cent. current efficiency) is suitable for use as a coulometer in the range of 0.1 to 3 coulombs. W. J. BAKER

**3551. Cells, apparatus and methodology for precise analysis by coulometry at controlled potential.** L. Meites (*Anal. Chem.*, 1955, **27** [7], 1116-1119).—The construction and operation of a direct-reducing current integrator (accurate and precise to  $\pm 0.1$  per cent.) and of two mercury-cathode cells suitable for rapid controlled-potential electrolyses are described. One cell is designed for electrolytic separations with a mercury cathode at controlled potential and an internal auxiliary electrode, and can be used for coulometric analyses when a suitable anodic depolariser can be found. The other, double-diaphragm, cell can be used for analysing solutions (e.g., of  $\text{Cu}^{II}$  in ammoniacal soln.) for which a suitable auxiliary electrode-depolariser combination is impossible to find. The general procedure for accurate analysis by coulometry at controlled potential is outlined. Determinations of from 2 to 600 mg of  $\text{Cu}^{II}$  are accurate and precise to within 0.1 per cent. An extrapolation technique for reducing the time of electrolysis to only 20 to 30 min. is described. W. J. BAKER

**3552. Portable high-frequency titrimeter.** J. P. Dowdall, D. V. Sinton and H. Stretch (*Analyst*, 1955, **80**, 491-498).—A stable, easily constructed battery-operated titrimeter with a tuned-anode-tuned-grid oscillator operating at 15 to 20 Mc.p.s.

is described in detail. Examples are given of its use for the determination of ionisable fluorine by titration with lanthanum acetate, titration of alkali with acid, titration of  $\text{Cl}^-$  with  $\text{AgNO}_3$  and of organic bases in non-aqueous media.

A. O. JONES

**3553. Amperometric instrument for quantitative determination of oxygen dissolved in oil-field brines.** F. E. Armstrong, R. J. Heemstra and G. W. Kincheloe (*Anal. Chem.*, 1955, **27** [8], 1296-1300).—The design, operation and calibration of an improved portable amperometric instrument for the rapid quant. determination of dissolved oxygen in brine samples are described and illustrated. The meter comprises a simple electrolysis H-cell (with S.C.E. and agar - KCl bridge), a rotating polished-platinum micro-electrode, a voltage supply, a micro-ammeter and a thermistor for measuring brine temp. The micro-electrode, sealed in soft-glass with mercury contact to the platinum wire, is rotated at  $\approx 600$  r.p.m., the applied voltage being  $-0.70$  V. The diffusion current of the micro-electrode is calibrated in terms of oxygen concn., using the modified Winkler method, whilst the effect of rate of change of ionic diffusion with temp. is corrected for by reference to curves for equiv. conductance - temp. coeff. change with temp. (at different concn. of NaCl). A glass-sealed platinised-platinum electrode can be used for pure, synthetic brines, but not for oil-field brines. The accuracy is  $\approx 5$  per cent. When analysing brines that have not been tested previously, comparison should be made with other methods because the amperometric apparatus can be sensitive to some other ions present.

W. J. BAKER

**3554. Some new vacuum technical and chemical applications of the radio-frequency mass spectrometer. I. Radio-frequency leak-detector.** Gábor L. Sebestyén and Péter F. Váradi (*Magyar Kém. Foly.*, 1955, **61** [2], 33-42).—After a survey of modern mass spectrometers, particularly as used for leak-detection, a simple leak-detector, based on Bennett's mass spectrometer, is described in detail. It can be incorporated into the system to be

examined. The spectrometer tube resembles a radio-receiving valve, and needs no separate pump. Leaks of  $< 0.05 \mu\text{l}$  per hr. can be detected. The time of response is 0.5 sec.

A. G. PETO

**3555. Routine energy measurements of soft radiations.** M. L. Curtis and J. W. Heyd (*Anal. Chem.*, 1955, **27** [7], 1073-1076).—Identification of one or more radio-isotopes in a mixture by determination of the energy of emitted particles with windowless absorption counters is discussed, and suitable instruments and procedures are described. The absorbers ( $0.02$  to  $1700$  mg per sq. cm in thickness) are placed inside a hemispherical proportional chamber, the distance between the base of the absorber and the sample being kept constant at  $0.05$  in. The very low energy-levels ( $0.03$  to  $0.15$  MeV) that can be measured are limited only by the thinnest absorbers (made from Formvar E film,  $0.02$  to  $0.10$  mg per sq. cm).  $\beta$ -Particles are distinguished from  $\alpha$ -radiation by changing the voltage setting. The energy of very soft  $\beta$ -particles (e.g., of  $29$  keV Ra-D), and also of hard  $\beta$ -particles, can be measured in the presence of  $\alpha$  radiation. The lead recoil atom from the  $\alpha$ -emission of  $^{210}\text{Po}$  has been identified by this procedure, whilst K-capture X-rays from  $^{56}\text{Fe}$  in a mixture of  $^{56}\text{Fe}$  and  $^{60}\text{Fe}$  can be identified. Accurate energy measurements of  $\alpha$ -emitters in a mixture are also possible (*Nucleonics*, 1955, **13** [5], 39).

W. J. BAKER

**3556. Electronics in paint testing.** Anon. (*Paint Manuf.*, 1955, **25** [6], 216-218).—An illustrated review is presented of apparatus shown at the Physical Society Exhibition, London, 1955, that is of interest to the paint industry. Among the exhibits described is an automatic apparatus for acid-alkali titrations, in which the burette is fitted with a two-speed tap controlled by a pH meter. The end-point can be set to any pH value to a precision of  $\pm 0.1$ , and the change from fast to slow flow can be arranged to anticipate the end-point by up to  $0.5$  pH unit.

D. R. DUNCAN

See also Abstracts 3325, 3368, 3415, 3454.



## ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current . . . . .	a.c.	millicurie . . . . .	mC
ampere . . . . .	amp.	milligram . . . . .	mg
Ångström unit . . . . .	Å	millilitre . . . . .	ml
anhydrous . . . . .	anhyd.	millimetre . . . . .	mm
approximate, -ly . . . . .	approx.	millimicron . . . . .	mμ
aqueous . . . . .	aq.	millivolt . . . . .	mV
atmospher-e, -ic . . . . .	atm.	minimum . . . . .	min.
boiling-point . . . . .	b.p.	minute (time) . . . . .	min.
British thermal unit . . . . .	B.Th.U.	molar (concentration) . . . . .	M
calorie (large) . . . . .	kg-cal.	molecul-e, -ar . . . . .	mol.
calorie (small) . . . . .	g-cal.	normal (concentration) . . . . .	N
centimetre . . . . .	cm	number . . . . .	no.
coefficient . . . . .	coeff.	observed . . . . .	(obs.)
concentrated . . . . .	conc.	ounce . . . . .	oz
concentration . . . . .	concn.	part . . . . .	pt.
critical . . . . .	crit.	patent . . . . .	pat.
crystalline . . . . .	{ cryst.	parts per million . . . . .	p.p.m.
crystallised . . . . .		per cent. wt. in wt. . . . .	per cent. w/w
cubic . . . . .	cu.	per cent. wt. in vol. . . . .	per cent. w/v
current density . . . . .	c.d.	per cent. vol. in vol. . . . .	per cent. v/v
cycles per second . . . . .	c.p.s.	potential difference . . . . .	p.d.
decompos-ing, -ition . . . . .	(decomp.)	pound . . . . .	lb
density . . . . .	ρ	precipitate . . . . .	ppt.
density, relative . . . . .	d or wt. per ml	precipitated . . . . .	pptd.
derivative . . . . .	deriv.	precipitating . . . . .	pptg.
dilute . . . . .	dil.	precipitation . . . . .	pptn.
direct current . . . . .	d.c.	preparation . . . . .	prep.
distilled . . . . .	dist.	qualitative, -ly . . . . .	qual.
electromotive force . . . . .	e.m.f.	quantitative, -ly . . . . .	quant.
electron-volt . . . . .	eV	recrystallised . . . . .	recryst.
equivalent . . . . .	equiv.	refractive index . . . . .	n <sub>D</sub>
experiment . . . . .	expt.	relative humidity . . . . .	R.H.
foot, feet . . . . .	ft.	revolutions per minute . . . . .	r.p.m.
gram . . . . .	g	saponification value . . . . .	sap. val.
gram-molecule . . . . .	mole	saturated calomel electrode . . . . .	S.C.E.
half-wave potential . . . . .	E <sub>1/2</sub>	second (time) . . . . .	sec.
horse-power . . . . .	h.p.	soluble . . . . .	sol.
hour . . . . .	hr.	solution . . . . .	soln.
hydrogen ion concentration . . . . .	[H <sup>+</sup> ]	specific gravity . . . . .	sp. gr.
hydrogen ion exponent . . . . .	pH	specific rotation . . . . .	[α] <sub>D</sub>
inch . . . . .	in.	square centimetre . . . . .	sq. cm
infra-red . . . . .	i.r.	standard temperature and pressure . . . . .	s.t.p.
insoluble . . . . .	insol.	temperature . . . . .	temp.
kilogram . . . . .	kg	ultra-violet . . . . .	u.v.
kilovolt . . . . .	kV	vapour density . . . . .	v.d.
kilowatt . . . . .	kW	vapour pressure . . . . .	v.p.
maxim-um, -a . . . . .	max.	volt . . . . .	V
melting-point . . . . .	m.p.	volume . . . . .	vol.
microcurie . . . . .	μC	watt . . . . .	W
microgram . . . . .	μg	wavelength . . . . .	λ
microlitre . . . . .	μl	weight . . . . .	wt.
micron . . . . .	μ		
milliampere . . . . .	mA		

In addition the following symbols are used—

greater than . . . . .	>	less than . . . . .	<
not greater than . . . . .	≥	not less than . . . . .	≤
is proportional to . . . . .	∝	of the order of, approximately . . . . .	~

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicals are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu<sup>+</sup>, Al<sup>+++</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>=-</sup>. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe<sup>III</sup> and cuprous copper Cu<sup>I</sup>.

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## CONTENTS

									Abstract
<b>General Analytical Chemistry</b>	..	..	..	..	..	..	..	..	3271
<b>Inorganic Analysis</b>	..	..	..	..	..	..	..	..	3287
<b>Organic Analysis</b>	..	..	..	..	..	..	..	..	3377
<b>Biochemistry</b>									
Blood, Bile, Urine, etc.	..	..	..	..	..	..	..	..	3413
Drugs .. ..	..	..	..	..	..	..	..	..	3456
Food .. ..	..	..	..	..	..	..	..	..	3475
Sanitation .. ..	..	..	..	..	..	..	..	..	3506
Agriculture and Plant Biochemistry	..	..	..	..	..	..	..	..	3513
<b>General Technique and Laboratory Apparatus</b>									
General .. ..	..	..	..	..	..	..	..	..	3520
Optical .. ..	..	..	..	..	..	..	..	..	3529
Thermal .. ..	..	..	..	..	..	..	..	..	3543
Electrical .. ..	..	..	..	..	..	..	..	..	3546

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 Acta Medica Scandinavica.  
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 Acta Physiologica Scandinavica.  
 Acta Vitaminologica.  
 Afinidad.  
 Agra University Journal of Research.  
 American Dyestuff Reporter.  
 American Ink Maker.  
 American Journal of Clinical Pathology.  
 American Journal of the Medical Sciences.  
 American Journal of Physiology.  
 American Journal of Public Health.  
 American Journal of Science.  
 American Paint Journal.  
 American Perfumer and Essential Oil Review.  
 American Society of Brewing Chemists Proceedings.  
 Anales de Bromatologia.  
 Anales de la Real Sociedad Española de Física y Química, Serie B.  
 Analyst.  
 Analytica Chimica Acta.  
 Analytical Chemistry.  
 Angewandte Chemie.  
 Annales de Biologie Clinique.  
 Annales de Chimie.  
 Annales d'Endocrinologie.  
 Annales des Falsifications et des Fraudes.  
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 Antibiotics and Chemotherapy.  
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 Arzneimittel-Forschung.  
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 Beiträge zur Biologie der Pflanzen.  
 Berichte der deutschen botanischen Gesellschaft.  
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 Biochemical Journal.  
 Biochemische Zeitschrift.  
 Biochimica et Biophysica Acta.  
 Bitumen, Teere, Asphalte, Peche.  
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 Branntweinwirtschaft.  
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 Brauerei.  
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 Brauwissenschaft.  
 Brennstoff-Chemie.  
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 Enzymolo  
 Erdöl und  
 Experiment

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  - Chemistry in Canada.
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  - Chimie Analytique.
  - Chimie et Industrie.
  - Chimie des Peintures.
  - Clinical Chemistry.
  - Coal Tar.
  - Collection of Czechoslovak Chemical Communications.
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  - Current Science.
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  - Drug Standards.
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  - Élelmezési Ipar.
  - Endocrinologie.
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  - Erdöl und Kohle.
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Journal  
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Kältetechnik  
Klinische  
Klinisch  
Kolloid-  
Konink  
Kunstst

Laborat  
Laborat  
Lancet.  
Lebensm  
Listy C

Magyar  
Meddel  
Medede  
Mellian  
Metal F  
Metall.  
Metallu  
Mikroko  
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Monats  
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Nafta [E  
Nationa  
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 Kunststoffe.
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 Laboratory Practice.  
 Lancet.  
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- Magyar Kémiai Folyóirat.  
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 Metallurgia.  
 Mikrochimica Acta.  
 Mitteilungen des chemischen Forschungs-Institutes der Wirtschaft Österreichs.  
 Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene.  
 Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.  
 Murex Review.  
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- Nafta [Yugoslavia].  
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 Naturwissenschaften.  
 Nederlandsch Tijdschrift voor Geneeskunde.  
 New Zealand Journal of Science and Technology, B.  
 Norges Apotekerforenings Tidsskrift.  
 Nucleonics.

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Österreichische Chemiker-Zeitung.  
Olii Minerali, Grassi e Saponi, Colori e Vernici.

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Paint Manufacture.  
Paintindia.  
Paliva.  
Paper Maker and British Paper Trade Journal.  
Papier [Darmstadt].  
Peintures - Pigments - Vernis.  
Petroleum Processing.  
Pharmaceutica Acta Helvetiae.  
Pharmaceutical Bulletin [Japan].  
Pharmaceutical Journal and Pharmacist.  
Pharmaceutisch Weekblad voor Nederland.  
Pharmazeutische Zentralhalle für Deutschland.  
Pharmazie.  
Phytopathologische Zeitschrift.  
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Science [New York].  
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South African Industrial Chemist.  
Spectrochimica Acta.  
Stärke.  
Studies in Conservation.  
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Sucrierie Française.  
Sugar [New York].  
Svensk Kemisk Tidskrift.  
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Sugar I  
Water I

## JOURNALS

Transactions of the American Association of Cereal Chemists.  
Transactions of the British Ceramic Society.  
Transactions of the Faraday Society.  
Transactions of the Indian Institute of Metals.

Ukrainskii Khimicheskii Zhurnal.  
U.S. Atomic Energy Commission, Reports.

Verfkroniek.

Wallerstein Laboratories Communications.  
Water and Sewage Works.  
Wissenschaftliche Beilage der Brauerei.

Zavodskaya Laboratoriya.  
Zeitschrift für analytische Chemie.  
Zeitschrift für angewandte Physik.  
Zeitschrift für Electrochemie und angewandte physikalische Chemie.  
Zeitschrift für Erzbergbau und Metallhüttenwesen.  
Zeitschrift für Lebensmittel-Untersuchung und -Forschung.  
Zeitschrift für Metallkunde.  
Zeitschrift für Naturforschung.  
Zeitschrift für Pflanzenernährung Düngung Bodenkunde.  
Zhurnal Analiticheskoi Khimii.  
Zhurnal Obshchei Khimii.  
Zhurnal Prikladnoi Khimii.

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## ACKNOWLEDGEMENTS

The organisations publishing the following journals are thanked for allowing reproduction of some abstracts.

British Baking Industries Research Association Abstracts.  
British Cotton Industry Research Association. Summary of Current Literature.  
British Food Manufacturing Industries Research Association Abstracts.  
Chemical Abstracts.  
Journal of the Institute of Metals.  
Journal of the Institute of Petroleum.  
Journal of the Iron and Steel Institute.  
Journal of the Textile Institute.  
Light Metals Bulletin.  
Nutrition Abstracts and Reviews.  
Paint Research Station Abstracts.  
Referativnyi Zhurnal, Khimiya.  
Sugar Industry Abstracts.  
Water Pollution Abstracts.

# ERRATA

## VOL. 1, 1954.

Abstract No.	Line
2438	2 for J. R. Riddick read J. A. Riddick.

## VOL. 2, 1955.

Abstract No.	Line
9	3 for W. West read P. W. West.
13	2 for Klinkersberg read Klinkenberg.
121	2 for V. Hagenström read U. Hagenström.
132	3 for Bohme read Böhme.
166	8 for up to read more than.
284	2 for A. H. Wilkins read D. H. Wilkins.
330	3 for Fitzgerald read FitzGerald.
532	2 for I read II. The formation of metal diethyldithiocarbamates and their extractability in relation to pH.
544	2 for Stöckle read Stöckli.
546	2 for II read VII.
574	2 for S. Holzbecher read Z. Holzbecher.
612	4 for L. Pungor read E. Pungor.
685	3 for Philipp read Philipp.
728	3 for F. H. Bruns read F. Bruns.
840	2 for J. P. Lodge read J. P. Lodge, jun.
918	3 for Boule read Boyle.
923	2 for M. Šušić read M. V. Šušić.
973	4 for J. du Ruisseau read J.-P. du Ruisseau.
1011	11 Insert "(apparent to unknown)" after "potency ratio."
1018	4 for Rapaport read Rapoport.
1100	2 for N. H. Addink read N. W. H. Addink.
1113	3 for III-V. III. read VIII.
1113	17 for IV read IX.
1113	23 for V read X.
1134	12 for VI read IV.
1157	3 for R. H. Rush read R. M. Rush.
1161	3 for Murate read Murata.
1246	2 for J. Barceló read J. R. Barceló.
1357	2 The abbreviation of the journal should be <i>Meded. LandbHogesch. Gent</i> .
1540	3 for E. Fujita read Y. Fujita.
1593	2 for Mapston read Mapstone.
1816	15 for cyanate read hydroxycyanide.
1856	2 for Thompson read Thomson.
1927	2 for Roquette read Rouquette.
1991	2 for B. J. Grunbaum read B. W. Grunbaum.
2081	22 for 0-0001 read 0-001.
2255	2 for Schlögel read Schlögl.
2291	3 for J. J. D. Walton read J. H. D. Walton.
2314	3 for Newald read Neuwald.
2481	16 for non-graphic read non-graphitic.
2482	2 for Roberts read Robert.
2633	2 for G. Wyld read G. E. A. Wyld.
2697	3 for S. Shinozawa read R. Shinozawa.
2710	2 for Todt read Tödt.
2866	2 for Okiyama read Okinaka.
The abstract after 2925 is wrongly numbered and should be 2926.	
3050	4 for Leddicote read Leddicotte.
3189	2 for Mahler read Maher.
3237	5 for dimethyl read diethyl.
3237	6 for diethyl read dimethyl.
3459	3 for Volkavá read Volková.
3467	2 for N. Knowlden read N. F. Knowlden.
3497	2 for C. R. Franzke read C. Franzke.

These include some errata subsequently published in the journals abstracted.



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